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Freezing, Melting, and Superfluidity of Helium in Porous Media

by

Eric Brian Molz



A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment
of the requirements for the degree of Doctor of Philosophy

in

Solid State Physics

Department of Physics

Edmonton, Alberta

Spring, 1995



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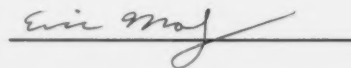
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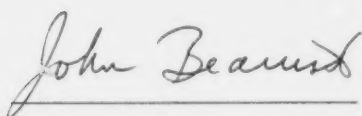
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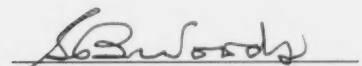
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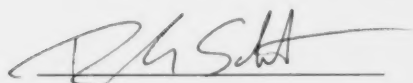
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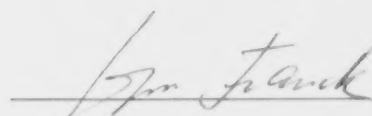
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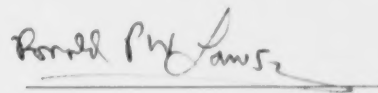
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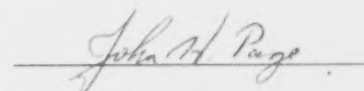
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DEDICATION

This dissertation is dedicated to my parents, Fredinand and Diane Molz.

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ABSTRACT

Ultrasonic velocity and attenuation measurements were made in helium-filled porous Vycor, silica aerogel, and Anopore Membranes using a phase-sensitive pulse-echo technique. These experiments investigated the behavior of freezing, melting, and superfluidity in these various microstructures. For helium in Vycor and silica aerogel, there is undercooling of the liquid phase, larger in Vycor with its smaller pores, and hysteresis between freezing and melting. The freezing curves of helium in Vycor and silica aerogel are very flat near absolute zero. There is a narrow pressure range where liquid and solid coexist at 0 K. Above these pressures, all the confined helium solidifies. The amount of superfluid does not decrease with pressure until freezing occurs in the pores. For helium in Anopore Membranes, there was no measurable undercooling or hysteresis between freezing and melting. This may be due, at least in part, to the pores being considerably larger than those in Vycor and silica aerogel and noninterconnected. Slight hysteresis is observed for lower pressures, where the melting curve is more flat. These results are compared to those of previous experiments and models of solidification and superfluidity in pores.

CHAPTER 1 - INTRODUCTION

The development of porous materials like Vycor glass (Corning "thirsty glass" 7930), aerogels, and Anopore Membranes (Anotec Inorganic Membrane Technology, Product Code 20021S) over the last thirty years filled a variety of industrial needs including moisture gettering, thermal insulation, and sensitive filtration. Further, their small pores (tens to thousands of angstroms in diameter) and large specific surface areas made them easy to fill with liquids. Adsorption measurements indicated that these materials fill at pressures below the bulk saturated vapor pressure. Soon, experiments [1] were being performed on the liquids confined in these small pores as they presented an opportunity to study finite-size systems. Experiments showed that phase transitions

such as freezing of liquids [1-19], superfluidity of ^4He [20-25], and more recently liquid-vapor critical points [26], and binary fluid phase separation [27-29] for these systems may be radically different from their bulk counterparts.

The freezing transition of several cryogenic liquids including argon [2], deuterium [3,4], helium 3 [5-7], helium 4 [7-14], hydrogen [4,15,16], neon [4], nitrogen [17], and oxygen [3,17,18] confined in porous media has been studied using heat capacity [2,4,8,11-13,15,19] torsional oscillator [14-15], light scattering [17-18], pressure [5-7,11-12], ultrasonic [2,9-10], and neutron scattering [3] measurements. Solidification in the pores is markedly different from that in bulk. The transition appears to be a continuous process over a finite temperature range, even for liquids with a triple point. In addition, the transition temperature itself is reduced, sometimes by as much as 15% of the bulk freezing temperature. Argon in Vycor at saturated vapor pressure is an example [2]. Freezing in the pores begins around 75.5 K, well below the triple point (83.8 K), and appears to complete around 72 K. This depression of the transition or undercooling may be related to its broadening. The amount of undercooling was found to depend inversely on pore size [5,7,19] and these media all have, to some degree, a distribution of pore sizes. The undercooling has an interesting effect on the phase diagram (Figure 1.1) of helium (any reference to "helium" throughout this dissertation implies ^4He unless otherwise stated). In bulk, liquid helium solidifies above 25 atmospheres at absolute zero. However, when confined in Vycor glass [10], liquid helium requires higher pressures to solidify. Thus helium can then exist as a liquid in pores at pressures above that of bulk. The helium in Vycor near the minimum pressure for solidification has not

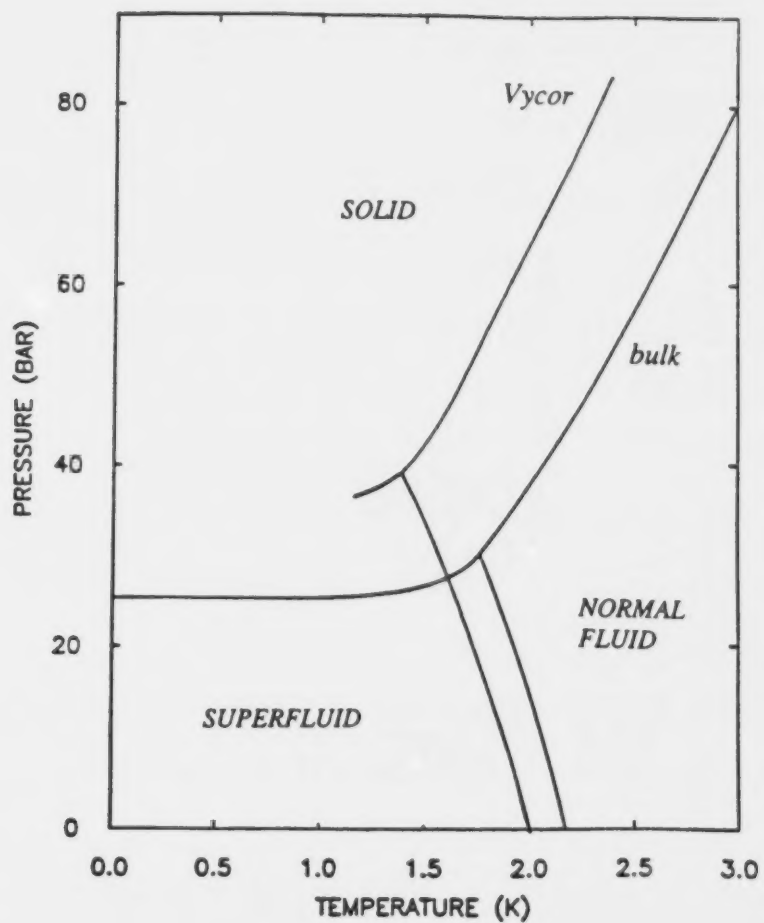


Figure 1.1 - Helium Phase Diagram in Bulk and Vycor

Both the melting curve and lambda line in Vycor are shifted from their bulk values (figure from Adams et al, 1986 [11]).

been intensely studied. Some questions concerning helium in Vycor include: what is the minimum pressure for solidification, at what minimum pressure, if at all, does freezing in the pores become complete, how flat is the melting curve at low temperatures?

Hysteresis between freezing and melting is observed when the experiment is thermally cycled, with melting temperatures closer to but still well below bulk. This indicates that the liquid is not simply being supercooled. Also, it has been demonstrated that the freezing process is completely irreversible [2] and displays "return point memory" similar to that seen in capillary condensation in Nucleopore Membranes [30]. This behavior is illustrated by sound attenuation in argon-filled Vycor [2] (Figure 1.2). Freezing in the pores begins at point B and continues as temperature is reduced. During the broad freezing process in the pores the cooling is halted at point C, then the system is warmed. The warming curve does not trace the freezing curve but rather follows a different path to point D. When cooled again, the new freezing curve follows the melting curve until the temperature where warming was initiated, point C. It then follows the original freezing curve. This is what is meant by return point memory.

Heat capacity measurements have yielded some interesting results. The measured latent heats of freezing and melting are less than for the same amount of adsorbate in bulk [2,12,15,17]. This, along with a roton-like heat capacity in hydrogen [15] and helium-filled [11] Vycor, has been considered as evidence that not all of the adsorbate freezes even at the lowest temperatures. On the other hand, neutron scattering experiments [3] show limited crystalline order for solid oxygen and deuterium in Vycor. Layers near the pore wall are strongly influenced by the amorphous glass and are highly

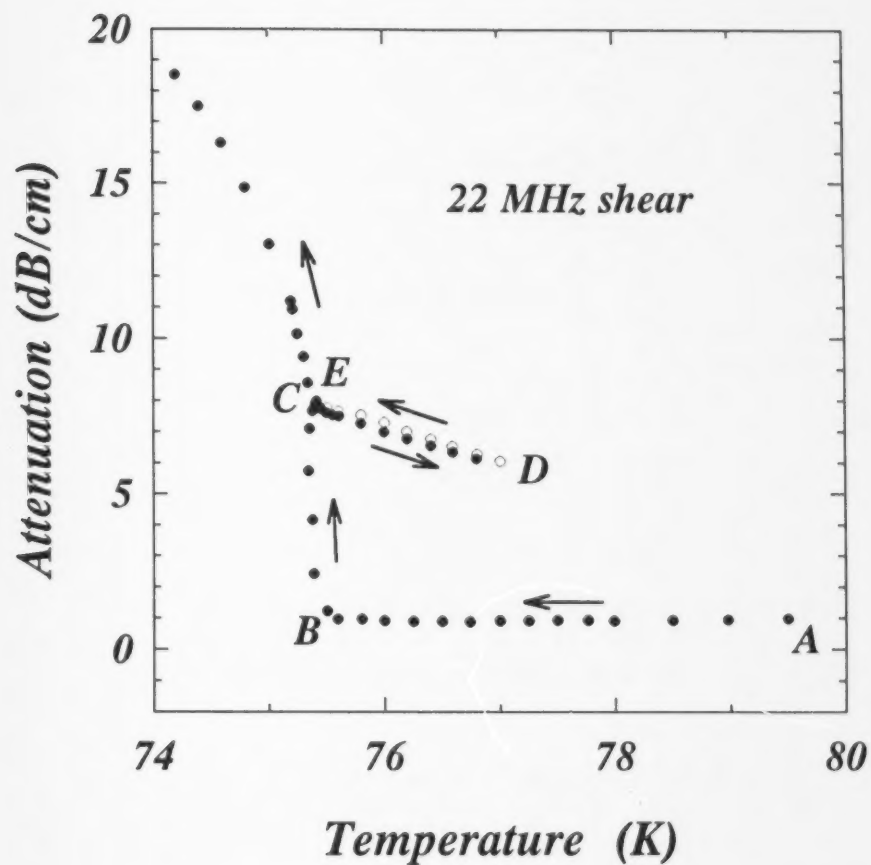


Figure 1.2 - Sound Attenuation of Argon-Filled Vycor

Sound attenuation demonstrates that the freezing process is irreversible and displays return point memory. Solid symbols are cooling data and open symbols are warming data. The cooling curve D-E traces the warming curve C-D (figure taken from Molz et al, 1993 [2]).

disordered. Long range order is restored over a healing length that may be nearly a pore size. This disordered layer does not participate in freezing and so does not contribute to the latent heat. This interpretation is supported by heat capacity data for hydrogen films adsorbed in Vycor [15]. Below a certain film thickness, no latent heat of freezing was observed.

Another puzzling result from heat capacity measurements [2,4,17] involved the relative size of latent heats of freezing and melting for fluids in porous glasses. Measured latent heats of melting (the area under the peak in the heat capacity curves) were larger than those of freezing. This appears to violate energy conservation since the system is brought back to its original state with no irreversible changes in the fluids or Vycor. The problem appears to be the experimental method, AC calorimetry [2]. In this technique, heat is continually added and taken away, even during cooling. Thus the temperature rises or falls with slight oscillations rather than monotonically. For an irreversible process like freezing in the pores, such oscillations can lead to a low latent heat value. During warming, however, the behavior is nearly reversible and the measured latent heat should be nearly correct.

Although theories exist, the mechanism for the hysteresis remains unclear. Arguments range from simple geometrical suggestions to more complicated pictures involving changes in the adsorbate near the pore wall or inhomogeneous nucleation in the Landau picture [31]. One goal of this dissertation is to experimentally study the relationship between irreversibility of freezing and melting and the pore structure. Clearly, an extensive study would include porous media of widely varying pore sizes and

shapes. Thus, freezing and melting have been studied in three porous media, Vycor, silica aerogel, and Anopore Membranes, and the results are reported in this dissertation. They encompass three vastly different microstructures that are characterized in Chapter 2.

Liquid helium will be used as the adsorbate for these experiments. The choice was fairly simple considering:

1. The freezing point is not fixed. Within a convenient pressure range (0 to 100 bar), the freezing transition can occur as high as 3 K or not at all.
2. The complete phase diagram for helium in Vycor includes both freezing and melting curves. The curves should be considerably different, with the melting curve closer to but not at the bulk curve.
3. At saturated vapor pressure, bulk liquid helium below 2.17 K undergoes a continuous transition from its normal state to a zero viscosity superfluid state. The superfluid transition temperature (as well as the superfluid fraction at any temperature) has pressure dependence (Figure 1) and is referred to as the lambda (λ) line. Detection of this continuous change can provide valuable

information as it signals the presence of liquid in the pores.

4) Helium holds considerable interest to physicists and, indeed, there is much comparative data for both solidification and superfluidity in pores. Still, experiments involving freezing helium in silica aerogel and Anopore membranes have not previously been performed.

Superfluidity in helium-filled Vycor and silica aerogels has been studied by torsional oscillator [14,24], heat capacity [20,25], thermal expansion [21], ultrasonic [22], and second sound [23] experiments. The lambda line (Figure 1.1) itself is suppressed in pores by an amount that increases with decreasing pore size. This, in combination with excess pressure required for solidification, allows superfluidity to occur above the bulk melting curve. Although the superfluid transition in Vycor is suppressed, the critical exponent for the superfluid fraction, ρ_s , is close enough to bulk (0.66 to 0.67) to suggest that the transition is three dimensional [25]. However, a much higher critical exponent (.81) has been measured in silica aerogels despite generally having pores larger than Vycor [23].

The experimental probe will be ultrasonic velocity and attenuation measurements using a phase-sensitive pulse-echo technique. This holds several advantages that merit individual discussion. First, ultrasonics is one of the few techniques (heat capacity measurements is another) that should be sensitive to both freezing and superfluidity in

the pores. To see this, consider that sound velocity of helium-filled porous media depends on the adsorbed helium's modulus and density. When helium in the pores solidifies, both the modulus and density increase. Prior work has demonstrated that solidification in Vycor is seen as a sharp increase in sound velocity [2]. With the onset of superfluidity, no real modulus or density change in the helium occurs. However, while the normal fluid fraction remains viscously locked to the motion of the pore wall, the superfluid fraction decouples, as would happen with a torsional oscillator. This change in the effective density is also seen as a sound velocity increase [9,21]. Sound attenuation monitors dissipation and provides complementary information. A more detailed description of sound propagation in helium-filled porous media at phase transitions is found in Chapter 2.

Secondly, this technique can explore frequency-dependence. It has been demonstrated [21] that the superfluid transition in Vycor is sharp at low frequencies and broadens and shifts to slightly higher temperatures as the frequency increases. Further, experiments [2,8] have shown that solid helium confined in Vycor will deform in response to mechanical stress with a characteristic time (τ) on the order of the frequency (ω), (that is, $\tau \sim 1/\omega$) at MHz frequencies. Thus, the apparent moduli of solid helium in Vycor are highly frequency-dependent. Specifically, at higher frequencies, where the sound period is shorter, the moduli of helium in Vycor appear larger.

Lastly, both shear and longitudinal modes can be produced. This becomes significant because media often transmit one mode significantly better. Further, the adsorbed liquid helium has a compressional modulus but no shear modulus. The freezing

transition (as well as superfluidity) may appear different for these two modes.

The dissertation is divided as follows. Chapter 2 is divided into two sections. Section 1 is divided into subsections on Vycor, silica aerogel, and Anopore Membranes for convenience. Each section details the production process, microstructures, and physical properties for each material. Section 2 presents the theory of sound in fluid-filled porous media, including plate modes for the Anopore Membranes. Chapter 3 is a brief description of the experimental components and technique including the ultrasonics, sample preparation, and the dilution refrigerator. Chapter 4 discusses models of freezing and superfluidity in finite-sized systems. Chapter 5 is a presentation and analysis of sound velocity and attenuation of helium during freezing, melting, and superfluidity in three porous materials. Chapter 6 is the summary.

CHAPTER 2 - POROUS MATERIALS

Porous materials are media with a considerable part of their total volume void. In the most restrictive cases, these voids may be extremely small, with at least one dimension less than a micron. Such porous materials include Vycor glass, aerogels and xerogels, Anopore and Nucleopore Membranes, sintered ceramics, and porous gold. Together, these form the majority of porous media in the study of finite-size systems. However, the production process for any one of these materials is unique and may produce a structure and pore geometry that is radically different from the others.

The propagation of sound in these helium-filled porous materials warrants a detailed presentation. The sound velocity in these is sensitive to changes in the adsorbed helium. To what degree the sound velocity responds is highly dependent on the material's microstructure. In fact, porous materials can be extensively characterized

simply from the behavior of the sound velocity during freezing and superfluidity of helium in the pores.

Chapter 2 is divided into two sections. Section 2.1 is an overview of parameters that characterize porous media followed by detailed subsections describing Vycor, silica aerogel, and Anopore Membranes. Section 2.2 begins with an introduction to the relevant length scales and discusses how their relative sizes determine the behavior of ultrasound in porous materials. Section 2.2 contains three subsections that describe the sound velocity changes due to the filling process, superfluidity and freezing of helium in the pores for the various pore geometries. A subsection on the acoustic modes in a plate waveguide is included in Section 2.2 to examine ultrasound propagation in Anopore Membranes.

Section 2.1 - Physical Characteristics

A porous material is described by several parameters that are mentioned throughout this dissertation: porosity, specific surface area, pore size and distribution, and tortuosity. Together, these parameters give a fairly complete description of a medium's microstructure and should be defined.

Porosity is simply the percentage of total volume that is void and can be easily determined comparing densities of the porous and solid forms. Another method to measure porosity involves measuring the sound velocity change from empty to filled

pores [32]. Some aerogels have been produced with porosities exceeding 99.8% and actually become difficult to see.

Specific surface area is the total surface area of the given material per unit mass and is determined to within a few percent by Brunauer-Emmett-Teller (BET) adsorption isotherms [33]. The highest specific surface areas may be nearly 1000 m² per gram for some aerogels [34]. BET measurements can be performed using ultrasonic sound velocity measurements [32].

Pore size usually refers to the smallest dimension of a typical pore. This parameter is of vital interest to the researcher since it often determines how radically the various adsorbate properties differ from bulk. The distribution of pore sizes in some materials can be surprisingly narrow. Mercury intrusion porosimetry [35] measures the size of the most restrictive void regions. In Vycor, these are the "bottlenecks" connecting pores. Mercury intrusion porosimetry measurements on Vycor found that basically all the "bottleneck" diameters are within 10% of the mean.

Tortuosity is an expression of the relative "twistiness" of a typical path through the porous material. It is numerically expressed as a path length through the media divided by the sample's geometric length; long straight pores extending from one end of the medium to the other have a tortuosity of unity. Tortuosity is usually a difficult parameter to measure. However, tortuosity can be determined using sound velocity measurements of superfluid helium-filled media. This technique is discussed in Section 2.2.

Vycor, silica aerogel, and Anopore Membranes give a wide range of porosity,

specific surface area, pore size, and tortuosity. Each was also well-suited for ultrasonics and readily available. The following subsections are a summary of the production processes, physical properties, and transmission electron microscope (TEM) pictures of Vycor, silica aerogel, and Anopore Membranes.

2.1.1 - Vycor

Vycor "thirsty glass" (Corning 7930) is produced by spinodal decomposition of a glass mixture into boron and silicon-rich phases. The boron-rich phase is acid-soluble and is leached away leaving a 96% silica (SiO_2) matrix. The remaining glass is highly resistant to breakage and can be used for adsorption of unwanted vapor such as moisture in the air.

Vycor glass (Figure 2.1.1 [36]) is often described as a network of cylindrical pores interconnected by bottlenecks. These bottlenecks are not very restrictive having nearly pore-size diameters. Vycor is typically 28% porous with a specific surface area of about 100 m^2 per gram [32]. Most pores sizes are within a few angstroms of the mean ($40 \text{ \AA}$ in this case). Vycor's tortuosity has been measured to be 4.1 [37].

The transverse sound velocity in Vycor is about 2000 m/s and is independent of orientation. Vycor glass lacks long-range order and has low temperature acoustic behavior [38] like other amorphous materials. Ultrasound in Vycor (Figure 2.1.2 [39]) has a frequency-dependent velocity peak and an attenuation plateau around 1 K due to

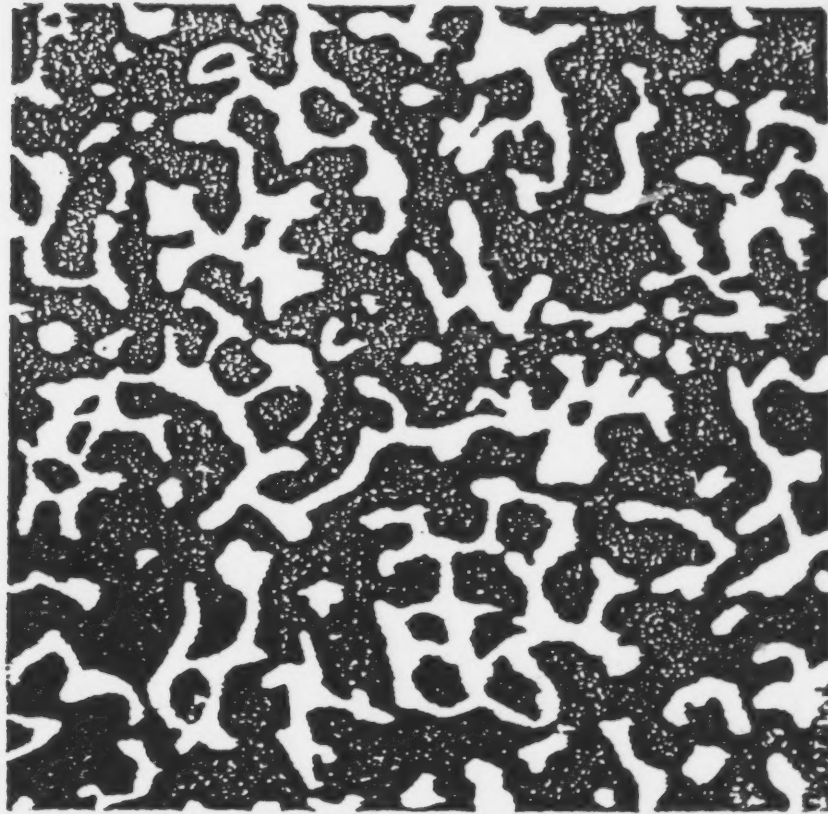


Figure 2.1.1 - TEM of Vycor

Digitally enhanced micrograph shows Vycor microstructure (figure by Levitz, Ehret, and Drake and shown in Khurana, 1989 [36]).

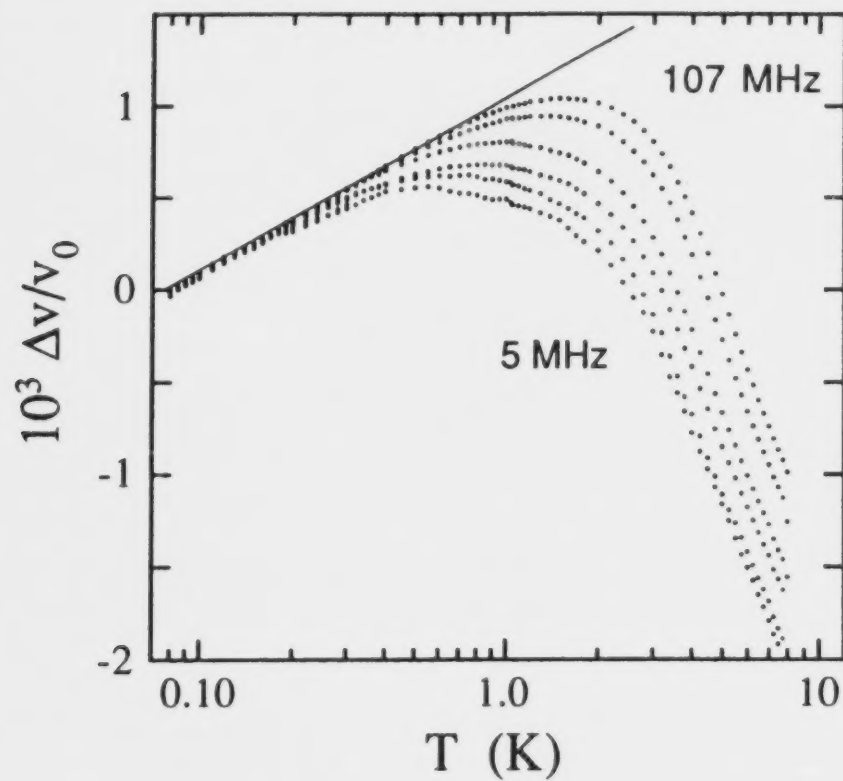


Figure 2.1.2 - Sound Velocity in Empty Vycor

Change in sound velocity in empty Vycor shows peak near 1 K and resonant and relaxation contributions (figure taken from Mulders et al, 1993 [39]).

a population of low-energy excitations, two-level systems (TLS). Two-level systems are sites with two accessible states corresponding to a potential minimum. These TLS interact with a passing sound wave through two distinct mechanisms: resonant and relaxation. The resonant interaction occurs when an acoustic phonon is emitted or absorbed during a flip between states. This results in a $\ln(T)$ dependence in sound velocity below the peak. The relaxation process occurs when the TLS population, out of equilibrium due to modulation by the sound wave, relaxes through interaction with thermal phonons. This is seen as the $-\ln(T)$ dependence above the peak. This active background from TLS in the glass should be visible even during freezing experiments. Acoustic properties of Vycor are also sensitive to adsorbed He^4 and He^3 films [39] since these change the TLS relaxation rates.

2.1.2 - Silica Aerogel

Silica aerogel can be produced from a TMOS sol-gel process that can easily be performed in an independent laboratory. During this process, silica (SiO_2) and methanol are produced from a reaction of tetramethylorthosilicate and water. Some methanol is initially added and determines the porosity. During gelation, silica spheres, usually 20 to 50 Å in diameter, cluster to form solid silica strands surrounded by liquid methanol. The silica skeleton that may be fractal for some aerogels [40] is hypercritically dried leaving a very open geometry that can hardly be considered an interconnected network

of pores (Figure 2.1.3 [41]). Rather it appears as large irregularly shaped voids.

Silica aerogels can be produced with porosities from 85 to over 99% and have surface areas as large as $1000 \text{ m}^2/\text{g}$ [34]. Thus they are useful as sorption getters and thermal insulators [41]. The void regions can have a wide range of sizes, from 20 to $1000 \text{ \AA}$. The tortuosity for this particular silica aerogel was measured to be 1.5 and the calculation is discussed in Section 2.2.

The ultrasonic sound speed and attenuation in silica aerogel is independent of orientation and is highly dependent on the porosity. Like Vycor, silica aerogel lacks long range order. However, the behavior characteristic of amorphous materials has not yet been observed in low temperature acoustic measurements. Shear velocities may be as low as 100 m/s in the most highly porous samples. To reduce sample attenuation, an 85% porous sample was chosen for experimentation with a shear sound speed of about 400 m/s .

2.1.3 - Anopore Membranes

Anopore Membranes (Anotec Inorganic Membrane Technology) are produced by electrochemically etching an oxide (Al_2O_3) layer grown on an aluminum substrate. The result is a 60 micron thick wafer with long, parallel pores perpendicular to the flat surface (Figure 2.1.4 [42]). The pores result from current paths during etching and extend the sample thickness. This manufacture process can be precisely controlled and

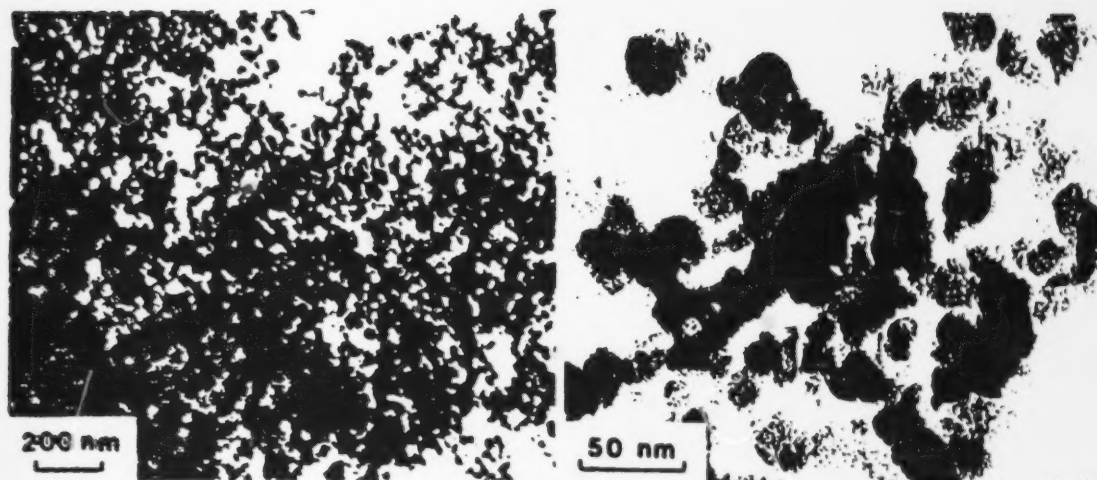


Figure 2.1.3 - TEM of Silica Aerogel

TEM micrograph shows silica aerogel microstructure (figure taken from Schreiber et al, 1985 [41]).

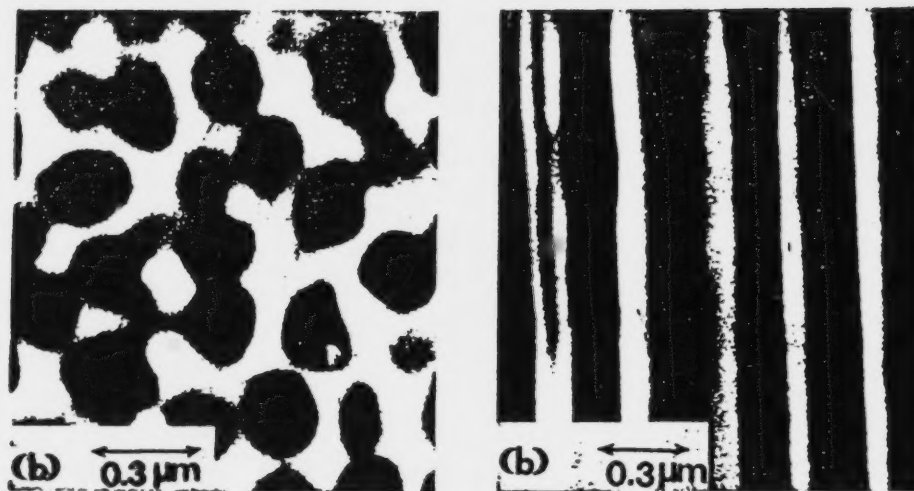


Figure 2.1.4 - SEM of Anopore Membrane

SEM micrographs show Anopore Membrane microstructure of the surface (right) and of the 60 micron-thick sides (left) (figure taken from Crawford et al, 1992 [42]).

very reproducible pore structures and orientations are obtained. Thus Anopore Membranes are used for sensitive filtration needs.

Anopore can be purchased in a variety of pore diameters. However, scanning electron microscope (SEM) pictures suggest [41] that the pore diameters quoted refer to the restrictive openings at the surface and that the interior of the pore is about 2000 Å for all samples. The pore size distribution appears to be very narrow and the pores are not interconnected. Anopore porosity is about 50% and specific surface area has been measured to be 7.5 m²/g [42].

Unlike Vycor and silica aerogel, pore orientation in Anopore Membranes is very anisotropic. Geometrically, the tortuosity of the pores is infinite in any direction contained in the flat plane of Anopore as the pores are perpendicular and not interconnected. However, along the axis normal to the membrane the tortuosity should be close to unity. In addition, Anopore may be considered a two-dimensional solid and ultrasound may propagate via a variety of "plate" modes. The sound velocity for a shear plate mode in Anopore is about 2500 m/s. Plate modes are discussed in Section 2.2.4.

2.2 - Ultrasound in Porous Media

Ultrasonics is a branch of acoustics that involves sound waves with frequencies above the audible range, accepted as 16,000 Hz. These waves may be in the form of longitudinal (compressional), shear (transverse), plate, rod, or surface modes. In these

porous media several of these modes may be excitable due to their widely varying solid structures. Further, once helium-filled, the behavior of various modes is strongly influenced by changes in the absorbed helium.

To determine how ultrasound propagates in helium-filled porous media, several length scales must now be introduced and compared. These are pore size (d_p), the ultrasonic wavelength (λ), sample size (D), and the viscous penetration depth (δ) of the confined liquid helium. Of these, only viscous penetration depth needs to be defined. Imagine stationary liquid helium in contact with a solid wall that is oscillating in its own plane. Liquid closer than the viscous penetration depth to the wall is dragged into the motion of the wall. However, liquid farther than the viscous penetration depth decouples and remains stationary. Therefore, the viscous penetration depth is a crossover length of coupled and decoupled liquid helium. A more detailed discussion of this quantity is provided in section 2.2.1.

Typical sizes for these quantities in these experiments are as follows. As mentioned before, pore sizes in these three media vary from about 40 to 2000 Å. Ultrasonic wavelengths in these porous media are on the order of 10^4 meters. All dimensions of the samples are at least a few millimeters except the thickness of the flat plane of the Anopore Membranes, which is only about 60 microns. The viscous penetration depth of the liquid helium is highly dependent on the frequency at which the wall is oscillated. The viscous penetration depth for liquid helium at saturated vapor pressure for ultrasonic frequencies can be tens to hundreds of angstroms.

The relative size of the ultrasonic wavelength and the pore size determines

whether the porous media can be treated as homogeneous medium. As ultrasound propagates through these porous media, considerable scatter from the pores would occur if the wavelength was on the order of a pore size ($\lambda \sim d_p$). A typical wavelength for ultrasonic frequencies is orders of magnitude larger than the pore sizes or grains of Vycor, silica aerogel, and Anopore Membranes. Thus, over a wavelength, the stress gradient is small and acoustical scattering from modulus or density mismatches associated with these boundaries is negligible and these porous media can be treated as homogeneous solids.

Every dimension for Vycor and silica aerogel samples is orders of magnitude greater than the ultrasonic wavelength ($D \gg \lambda$). Thus, these can be considered three-dimensional solids and bulk longitudinal and shear sound modes are excited. Longitudinal waves have solid displacement in the direction of the wave vector. Over one wavelength, regions of solid are alternately compressed and expanded. Hence the mode is also termed "compressional". Conversely, solid displacement for shear waves is normal to the wave vector. In this slower-moving mode, layers of solid move up and down over one wavelength with no local density variations. A given wavevector can have two shear modes, one for each perpendicular axis. Meanwhile, Anopore Membranes have thickness comparable to the ultrasonic wavelength and may belong to a class of solids called acoustic waveguides. In a waveguide, sound propagation is parallel to the major surfaces of the media. In the case of a two-dimensional plate, the wavevector must be in the plane of the membrane. The direction of solid displacement, however, depends on the plate mode excited and is generally more complicated than that

in bulk modes. Three plate modes need be considered: shear, longitudinal, and flexural. These modes will be discussed in detail in Section 2.2.4.

The relative size of the pore and the viscous penetration depth of helium determines if a portion of the confined helium is independent of the motion of the solid matrix. For $\delta \gg d_p$, all helium is viscously locked into the motion of the pore wall and the helium-filled porous medium acts as a single effective medium. Conversely, for $d_p > \delta$, the helium has two components: the fraction against the pore wall that is viscously locked and the rest that has decoupled. Further discussion of the decoupling of helium from the various pore geometries of these materials is found in Section 2.2.1.

Vycor and aerogel, unlike Anopore Membranes, are very isotropic. That is, there is essentially no gradient in pore sizes or shapes and samples can be prepared independent of orientation. Anopore Membranes, as well as being plate-like, are very anisotropic. Recall that the pores in Anopore extend the entire membrane thickness and are nearly perpendicular to the flat plane. Thus, the orientation of the pores with respect to solid displacement must always be considered.

To repeat, Vycor, aerogel, and Anopore Membranes can be treated as homogeneous solids. Bulk longitudinal and shear modes are excitable for Vycor and silica aerogel while Anopore Membranes belong to a class of solids called acoustic waveguides and support plate modes. Vycor and aerogel are isotropic solids while Anopore Membranes are highly anisotropic.

Section 2.2 is divided into three subsections on sound velocity changes from filling the pores and, once filled, superfluidity and freezing of helium in the pores and

includes a subsection describing the "plate modes" in Anopore Membranes and their response to phase transitions in pores. The behavior of the sound velocity during phase transitions can be a sensitive method of characterizing physical aspects of porous materials since the transition is effected by the material's microstructure. Of course, simply filling pores with helium can hardly be considered a phase transition. However, it requires consideration of some aspects that are important to understanding later parts of this dissertation.

2.2.2.1 - Filling Pores

The velocity of a shear stress wave in an empty isotropic porous medium is

$$V_s = \sqrt{\frac{\mu_p}{\rho_p}}, \quad 2.1$$

where μ_p and ρ_p are the empty medium's shear modulus and density. Now, in the presence of helium at its saturated vapor pressure (SVP), the pores fill completely with liquid helium. Any change in sound velocity is due to helium contributions to the overall shear modulus (and bulk modulus in the case of a longitudinal wave) and density.

A helium contribution to the overall shear modulus is due to a rigid response to

distortion of the pore. However, any stresses in the liquid-filled pore relax via viscous flow. Treating the pore as a cube, the characteristic relaxation time is of order η/K , where η and K are helium viscosity and bulk modulus. Using values for liquid helium at 4.2 K and SVP (1 atm), $\eta \approx 3.6 \times 10^{-6}$ Pa-sec and $K \approx 4.6 \times 10^6$ Pa⁻¹, yields a relaxation time of 7.8×10^{-13} sec, much shorter than an ultrasonic period. Thus, the liquid helium displays essentially no rigidity and makes no contribution to the overall shear modulus. (The helium in the pores would, however, increase the overall bulk modulus as the liquid supports longitudinal sound). In order for the liquid helium to contribute to the system density, the liquid must become viscously locked into the motion of the pore wall. To illustrate, imagine a fluid in contact with an infinite wall in the x-y plane oscillating in the y-direction. The fluid oscillates with the wall but dampens exponentially in the z-direction. The amplitude decreases by a factor of e^{-1} at a distance from the wall

$$\delta = \sqrt{\frac{2\eta}{\omega\rho_f}}, \quad 2.2$$

where η and ρ_f are the fluid viscosity and density and ω is the angular frequency of oscillation. For a fluid-filled porous material with pore sizes significantly smaller than this aforementioned "viscous penetration depth" (δ), the liquid is viscously locked to the pore surface and the full density contribution is observed. Similarly, this condition is

satisfied for a given pore size (d_p) if the frequency is smaller than the "critical frequency" (ω_c) expressed as

$$\omega_c = \frac{2\eta}{\rho_f d_p^2} \quad 2.3$$

For helium-filled Vycor with 40 Å pores at 4.0 K and SVP, the critical frequency is 600 MHz. Ultrasonic frequencies higher than 100 MHz are seldom excited in Vycor so that the "low frequency regime" is observed. The sound velocity for helium-filled Vycor therefore becomes

$$V_s = \sqrt{\frac{\mu_p}{\rho_p + \phi \rho_{He}}} \quad 2.4$$

where ϕ is the porosity and ρ_{He} is the density of the helium in the pores. Silica aerogel and Anopore Membranes, even though the frequency range is restricted to 15 MHz or less, may serve as examples of the "crossover regime" and the "high frequency regime". With 400 Å and 2000 Å pores, the critical frequencies are 6 MHz and less than 1 MHz, respectively. In the latter case, only a small fraction of the adsorbed helium density, ρ_{He} may contribute to V_s as most helium remains stationary. This "sloshing" in the high

frequency regime is the mechanism for sound attenuation in Biot theory.

2.2.2 - Superfluidity in Pores

In pores, like in bulk, there is a critical temperature T_c for the onset of superfluidity. At every temperature below the critical temperature, T_c , the helium has associated normal and superfluid components. That is,

$$\rho_{He} = \rho_n + \rho_s . \quad 25$$

The zero viscosity superfluid component has no viscous penetration depth so that, at any frequency, superfluid will decouple from the motion of the pore wall. Only the normal fluid contributes to the effective density of the liquid helium. The signature of the onset of superfluidity in the pores is a sharp increase in sound velocity due to this decrease in the effective density. The sound velocity continues to increase until the helium is essentially all superfluid.

Below 1 K, the normal fluid component is essentially gone and $\rho_{He} = \rho_s$. One might figure that the sound velocity of superfluid helium-filled porous material is about the same as that of empty porous material. This argument, however, ignores the inertial

effect that tortuosity can provide. While it is true superfluid helium cannot be "dragged" into motion by viscosity, a highly tortuous geometry can "push" superfluid helium into moving with the solid. In an isotropic porous medium, the fraction of superfluid that decouples at any temperature below T_c is less by a factor of $1/C$, where C is the tortuosity. The effective helium density, assuming all the normal fluid is viscously locked to the solid, is then

$$\rho_n + (1 - \frac{1}{C})\rho_s . \quad 2.6$$

The sound velocity, accounting for superfluidity and tortuosity effects, is expressed

$$V_s = \sqrt{\frac{\mu_p}{\rho_p + \phi(\rho_n + (1 - \frac{1}{C})\rho_s)}} . \quad 2.7$$

For helium in Vycor, this effect has been studied experimentally [37]. Well below 1K, $\rho_n = 0$. However, 78% of the helium still contributes to the overall density, yielding a tortuosity of 4.1. Tortuosity of this particular silica aerogel has been measured during the course of this research. Assuming a critical coverage that does not

become superfluid of 28 micromoles per square meter [37], the same as Vycor, a tortuosity of 1.5 was measured. In the case of either Vycor or aerogel, substantial amounts of normal fluid couples and superfluid decouples making superfluidity easily distinguished ultrasonically.

Decoupling of superfluid helium in anisotropic media like Anopore Membranes is more complicated and depends on the motion of the sample with respect to the orientation of the pores. Consider an Anopore Membrane filled with superfluid helium. If one were to oscillate the membrane normal to its flat surface, essentially all the superfluid should decouple from this motion. Conversely, if the membrane were oscillated in its own plane, the superfluid is expected to couple to this motion and the majority of its density should contribute to the effective density.

2.2.2.3 - Freezing in Pores

During freezing in the pores, solid helium contributes to the system's modulus as well as its density. Assuming all the helium solidifies, the sound velocity becomes

$$V_s = \sqrt{\frac{\mu_p + \Delta\mu_{He}}{\rho_p + \phi\rho_{He}}} \quad 2.8$$

where $\Delta\mu_{He}$ and $\phi\rho_{He}$ are the shear modulus and density contributions of solid helium. To predict the sound velocity response, the modulus and density terms will be examined separately.

The shear modulus contribution of helium in the pores can be estimated in analog to the compressional modulus contribution as [2]

$$\Delta\mu_{He} = \frac{1}{\phi} \left(1 - \frac{\mu_p}{\mu_s} \right)^2 \mu_{He} , \quad 2.9$$

where μ_s is the shear modulus of the solid component of the porous medium in a nonporous form. This approximation takes into account that the strain in the porous medium and in the helium are not the same and is applicable for a porous medium where the strain in the pores is expected to be nearly uniform (like Vycor and unlike aerogel). It also assumes that the modulus is small compared to that of the porous medium. That is, the "rigid frame" limit. To predict the sound velocity response to freezing in pores, consider Vycor. Using 2.3×10^{10} Pa, 8.5×10^9 Pa, and 2.5×10^7 Pa for the solid Vycor, porous Vycor, and solid helium shear moduli at 50 bar, respectively, the shear modulus contribution of the solid helium is 7.6×10^7 Pa. This increases the shear modulus about 0.90%.

To calculate the density contribution of solid in the pores, recall that the liquid density must be subtracted. The density of porous Vycor is 1.56 g/cc and the densities

of liquid and solid helium at 50 bar are 0.192 g/cc and 0.204 g/cc, respectively. Thus, the system density changes about 0.21%. Thus, freezing helium in Vycor should be seen as a shear sound velocity increase. Similar behavior is expected for aerogel and Anopore.

2.2.4 - Plate Modes in Anopore Membranes

Anopore Membranes can be approximated as two-dimensional solids as they have two large dimensions and one generally smaller than an ultrasonic wavelength. In two-dimensional solids, ultrasound propagates via plate modes that have somewhat different behavior than bulk modes. To describe these possible plate modes, coordinate axes with respect to the membrane should be assigned (Figure 2.2.1). The membrane is oriented in the plane defined by the x- and y-axes with the direction of the wavevector always along the x-axis. The z axis is then normal to the Anopore surface. For a plate of thickness "b", the boundaries are at $z = \pm b/2$. The plate is infinite in the x and y directions.

The shear mode is characterized by solid motion only along the y-axis, normal to the wave vector. The shear mode is divided into two classes: symmetric and asymmetric. In the symmetric case, the stresses and resulting strains at $\pm z$ have the same magnitude and direction. In the asymmetric case, the stresses and resulting strains have the same magnitude and are in opposite directions. The dispersion relation [43] is

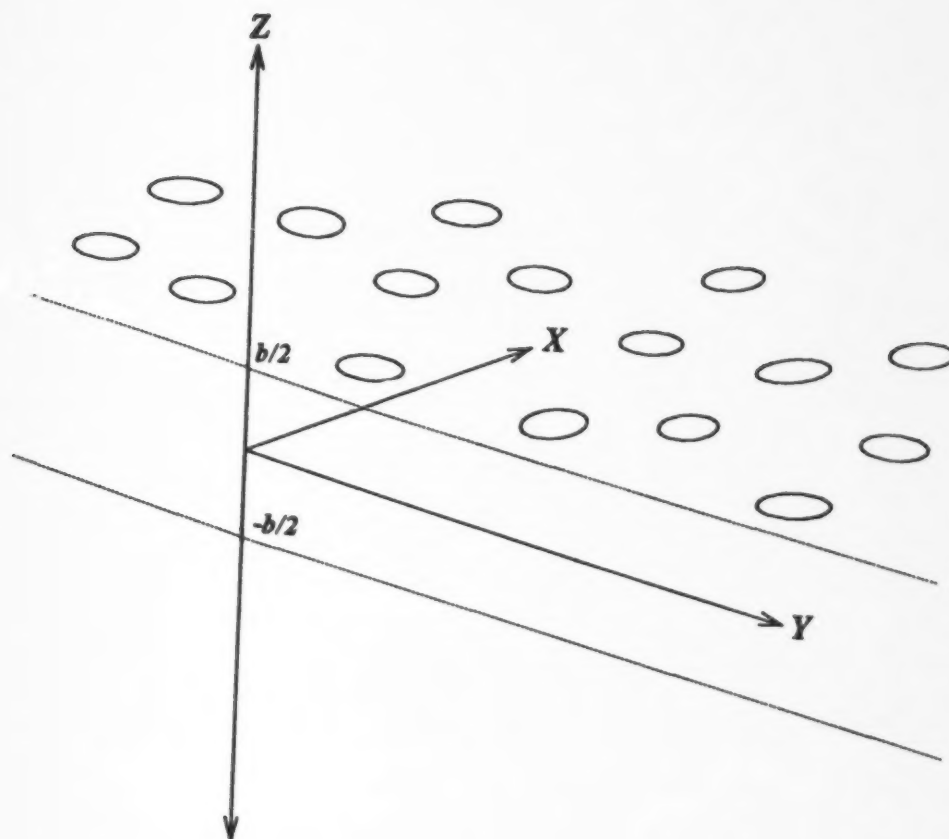


Figure 2.2.1 - Coordinates for Anopore Membrane

The coordinate axis are shown. The plate has boundaries at $z = \pm b/2$ and is infinite in x and y directions. The wavevector is always along the x axis.

$$\frac{\omega^2}{V_s^2} = k^2 + \frac{(\pi r)^2}{b^2}, \quad r=0,1,2,3\dots, \quad 2.10$$

for the symmetric shear mode and is

$$\frac{\omega^2}{V_s^2} = k^2 + \frac{(\pi r)^2}{b^2}, \quad r=1/2,3/2,5/2\dots \quad 2.11$$

for the asymmetric shear mode where ω is the angular frequency, k is the magnitude of the wave vector, V_s is the bulk shear velocity, and r defines the order of the mode. Thus symmetric shear modes of order r are expressed as SH(r) and asymmetric shear modes of order r are expressed as AS($r-1/2$). The frequency associated with SH(1) in the small thickness ($b/\lambda \rightarrow 0$) limit is

$$\omega = \frac{V_s \pi}{b}. \quad 2.12$$

Estimating the "bulk" Anopore shear sound speed to be about 3000 m/s, the frequency

of SH(1) for 60 micron thick Anopore is at least 250 MHz. Experimental frequencies are an order of magnitude lower. Thus, in this small thickness regime, the only symmetric or asymmetric shear mode excited is the nondispersive SH(0) mode.

The longitudinal and flexural modes are classified together as Lamb waves. In these modes, the membrane is stressed and can relax laterally so that solid moves in both the x- and z-directions. Sound propagation therefore has coupled shear and longitudinal components. Like the symmetric and asymmetric shear modes, longitudinal, L(r), and flexural, F(r), modes describe two types of compression and expansion along the x-axis: symmetric and asymmetric. In the symmetric or longitudinal case, regions at $\pm z$ are under equal stress. The result is lateral contraction and swelling of the Anopore. In the asymmetric or flexural mode, regions at $\pm z$ are under equal but oppositely directed stress. The result is bending or flexing of the Anopore as the sound wave passes. Solid displacement for the lowest order longitudinal L(1) and flexural F(1) modes are displayed in Figure 2.2.2. Notice that for the L(1) case the motion in the middle of the plate is wholly longitudinal while for the F(1) case the motion in the middle of the plate is wholly transverse. As either the upper or lower boundary is approached, the solid displacement has both longitudinal and transverse components.

Because there are two nonzero strain components, the dispersion relations for longitudinal and flexural modes are more complicated than those for the shear modes and have never been obtained in an analytical form. However, as $b/\lambda \rightarrow 0$, the sound velocity of the flexural mode approaches zero. This is demonstrated when a two centimeter-long Anopore sample is held stationary at one end and "plucked" at the other.

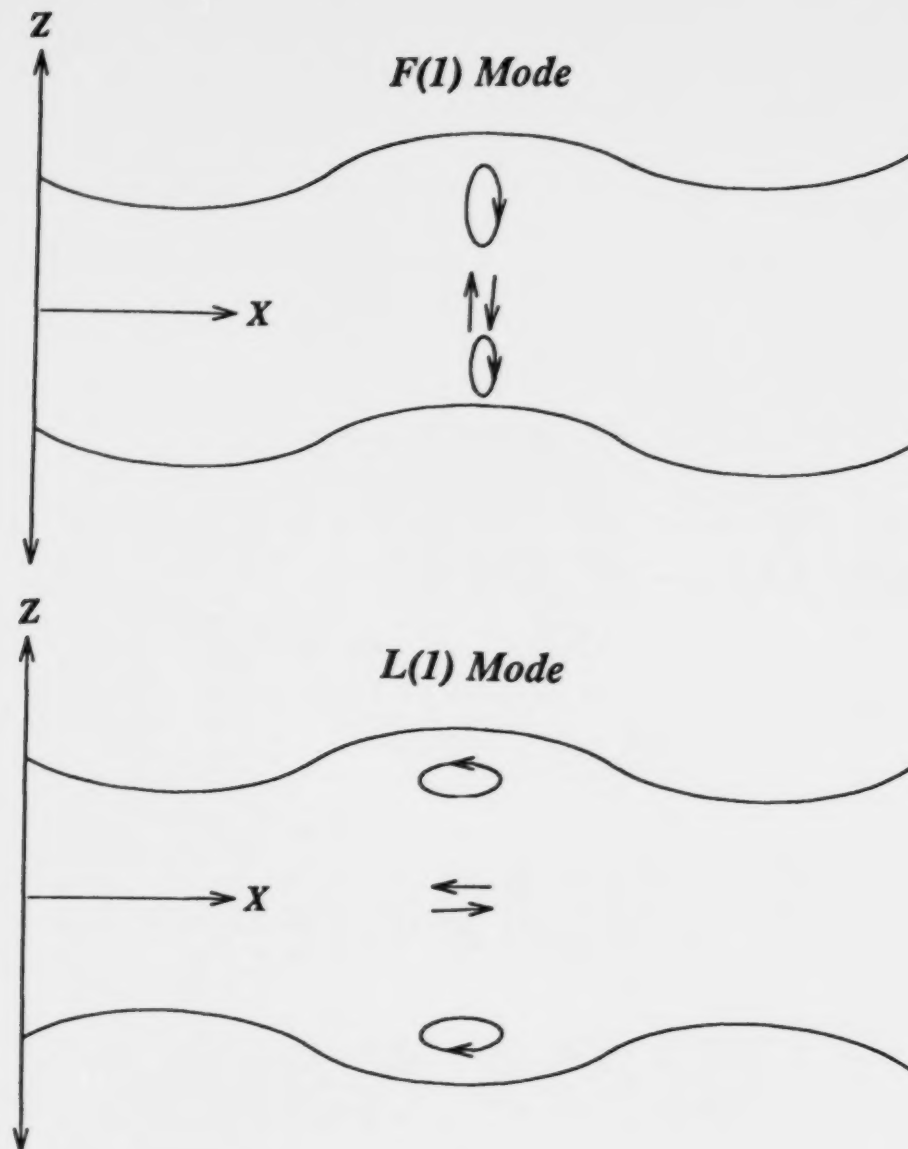


Figure 2.2.2 - Solid Displacement for L(1) and F(1) mode.

The solid displacement for the L(1) and F(1) mode are shown. For the L(1) mode, the motion is longitudinal at $z = 0$ with shear and longitudinal components away from $z = 0$. For the F(1) mode, the motion is shear at $z = 0$ with shear and longitudinal components away from the middle.

The membrane vibrates visibly indicating a very slow sound speed, perhaps a few meters per second. Thus, all flexural modes can be ignored. In the small thickness limit similar to the shear modes, only the essentially nondispersive lowest order of the longitudinal modes, $L(1)$, can be excited.

To repeat, bulk shear and longitudinal waves are easily excited for Vycor and silica aerogel. Anopore Membranes, treated as plate waveguides, should excite similar modes. Only the lowest order essentially nondispersive shear, $SH(0)$, and longitudinal, $L(1)$, waves are expected.

Due to their anisotropy, the total density contribution of liquid helium filling the pores of Anopore Membranes should depend on the mode excited. Recall that this situation is described by the "high frequency regime" where a considerable fraction of the liquid in the pores is not viscously locked to the motion of the pore wall. However, from the geometrical definition, the tortuosity for the $SH(0)$ modes in Anopore Membranes approaches infinity. With the large tortuosity for the modes of study, nearly the full density contribution should be observed. Since, the $L(1)$ mode has a shear component in the z -direction some decoupling may occur. The tortuosity for any flexural mode would be nearly 1, but again these modes have sound speeds too low to study. There is another possible mechanism for the decoupling of liquid helium only in the $L(1)$ mode. Since the pore is compressed, liquid may exit either end via "squirting". The characteristic time for such a process can be roughly calculated by expressing the pressure (dP) increase as a function of the compression of the pore by an amount dV :

$$dP = -\frac{1}{V\kappa}dV, \quad 2.13$$

where V is the pore volume and κ is the adiabatic compressibility of the fluid. This expression is then combined with the hydrodynamic equation for the steady state flow rate ($\Delta V/\Delta t$) of an incompressible liquid with viscosity η through a tube of length l and diameter a with a pressure gradient ΔP across it:

$$\frac{\Delta V}{\Delta t} = -\frac{\pi a^4}{8\eta} \frac{\Delta P}{l}. \quad 2.14$$

Treating a pore as a cylinder, the characteristic relaxation time can be expressed as

$$\tau = \frac{8\eta\kappa l^2}{a^2}. \quad 2.15$$

Using 1000 Å for the pore radius, 30 microns for the length, 3.6×10^{-6} Pa-sec for the helium viscosity, and 5×10^{-8} Pa⁻¹ for the helium adiabatic compressibility yields a characteristic time on the order of 10^{-8} seconds. This is at least as short as $1/\omega$ at

ultrasonic frequencies so that the squirting process may be a possible mechanism for the decoupling of helium in the L(1) mode. However, equation 2.14 is for the limiting case of an incompressible fluid. Flow for a highly compressible fluid like helium would be slower. In fact, the time for sound to travel the length of the pores in helium, certainly the lower bound of τ , is about 1.2×10^{-8} seconds, on the order of that calculated via equation 2.15. Also, in the high frequency limit which describes ultrasound in helium-filled Anopore, Biot theory [44] predicts that the effective permeability of the porous media can be significantly reduced, further limiting flow.

To summarize, only the nondispersive SH(0) shear and L(1) longitudinal modes should be excited in Anopore Membranes. Although the pore size is considerably larger than the helium viscous penetration depth, most helium density should be observed because of the large tortuosity for these modes. However, due to squirting of liquid helium from the pores during compression, some decoupling may be seen in the L(1) mode. This may be extremely important in studying the lambda transition in Anopore as some superfluid may decouple via this process.

CHAPTER 3 - EXPERIMENT

The experiments described herein can be divided into three main facets that function in unison: the sample, the ultrasonic spectrometer, and the dilution refrigerator. Each has its own purpose for low temperature ultrasonic experimentation. The desired sample must be properly prepared with LiNbO_3 transducers and produce a quality signal. The ultrasonic spectrometer generates and gathers ultrasonic sound velocity and attenuation data from the sample. The dilution refrigerator provides the low temperature environment for the sample. Failure of any one of these immediately halts work. The remainder of this chapter is divided into following sections: sample preparation including subsections on Vycor, silica aerogel, and Anopore, the ultrasonic spectrometer, and the dilution refrigerator.

Most of the equipment described in this section is left from the previous work of

Mulders [37]. The lack of major changes in this equipment is a testament to the quality of the systems. A very detailed discussion of the ultrasonic spectrometer and computer control has already been given [37]. This dissertation will include only a brief description of its operation and specifications.

3.1 - Sample Preparation

Sample preparation for the various porous materials is highly dependent on the physical characteristics wanted. Therefore preparation of Vycor, silica aerogel, and Anopore Membranes will be discussed separately. Once prepared, a sample has two transducers bonded on opposite faces as parallel as possible. One transducer acts as the transmitter of ultrasound and the other as the receiver. In this way, an electrical pulse is converted to an acoustic wave, propagates through the sample, and is converted back to an electrical pulse.

The choice of transducers and sample length is made with some consideration. The transducers, LiNbO_3 in every case, vibrate at frequencies from a few MHz to about 20% above their fundamental and can also be excited at odd harmonics of the fundamental. Depending on the crystal orientation when cut, these transducers are manufactured to produce shear or longitudinal waves in the sample. Although the shear mode is preferred, the received signal from the longitudinal mode is often much larger. The length is usually made as small as possible to reduce the total attenuation. At the

same time, the sample must be long enough to allow for a transit time for an ultrasonic sound wave greater than the pulse length. The reason for this restriction will be discussed in Section 3.2.

3.1.1 - Vycor

Vycor is sold in long cylinders 0.36 centimeters in diameter. A sample is cut to the desired length using a diamond wheel with little concern about the exact orientation of the two ends. Polishing the ends is a two step process using fine-grit sandpaper and then emery paper. The ends should be as flat and parallel as possible.

Vycor adsorbs contaminants from the air that, over the course of years, cover its surface. The sample is cleaned with consecutive hour-long baths in a 30% solution of boiling hydrogen peroxide, methanol, and distilled water. Once cleaned, Vycor regains its original transparency.

High viscosity silicone oil (Dow Corning 20000 Fluid) was used as the bonding agent for the transducers instead of an epoxy. The advantages of using grease are that the transducers can be reused and, more importantly, odd harmonics of the fundamental frequency seem to be transmitted better. There are, however, some disadvantages. The signal cannot be tested at room temperature as the oil solidifies around 100 K. The Vycor cannot be warmed and cooled as the bond deteriorates with each cycle. The Vycor must be carefully mounted with transducers pressed against the polished faces.

Mounting of Vycor in the ultrasonic cell insert is shown in Figure 3.1. The transducers are pressed against the Vycor using spring-loaded pins and oriented such that their axis of displacement is parallel. Once mounted and sealed into the ultrasonic cell, the Vycor is quickly cooled to 77 K. All experimentation in this dissertation was done on a piece of Vycor 1.37 centimeters in length using 28 MHz shear transducers.

3.1.2 - Silica Aerogel

Aerogel was prepared with some care. The delicate microstructure made polishing and cleaning of the aerogel impossible. Thus samples had to be cut with ends as parallel as possible. To do this, a Dremel high speed drill and cutting attachment were held stationary. A large piece of aerogel was then precisely positioned and moved into the blade for flat, parallel slices.

The choice of sample length and transducers was an interrelated problem. The samples had to be made as short as possible due to the large ultrasonic attenuation associated with freezing in the pores. Meanwhile when a sample was prepared with shear transducers, a longitudinal mode was visible. For samples with short transit times, the shear and longitudinal pulses overlap. The best solution was to use longitudinal transducers, as no shear mode was present, and as short a sample as possible.

Transducers were bonded using Bipax 2101 blue epoxy since oil would cause fractures where absorbed and high sample attenuation limits the frequency range to below

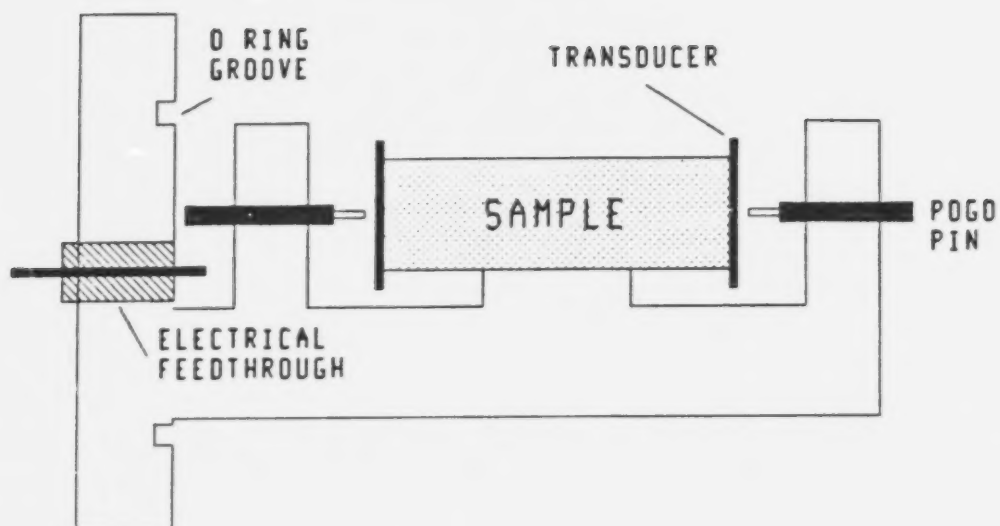


Figure 3.1 - Ultrasonic Insert

Samples are mounted between two LiNbO_3 transducers in the ultrasonic insert. The insert, which is about half the size of that depicted, then seals to the cell on the dilution refrigerator.

15 MHz anyway. The aerogel sample signal could then be checked at room temperature and thermally cycled. Mounting in the ultrasonic cell insert was then trivial as the aerogel was left supported only by its leads. All experimentation was done using a 0.29 centimeter piece of aerogel and 20 MHz longitudinal transducers.

4.1.3 - Anopore Membranes

Most aspects of the preparation of Anopore Membranes must be done with extreme care as they are very thin and brittle. The only successful method of making the desired rectangular pieces involved supporting the Anopore throughout the cut. This was accomplished by clamping the membrane between a magnet and an iron cover with the appropriate dimensions. The sample was then cut by tracing around the iron cover using the same technique as with aerogel. No attempt was made to clean the Anopore.

The most complete study would include both the shear SH(0) and longitudinal L(1) plate modes. Shear transducers oriented so that shear displacement is in the plane of the Anopore excite the SH(0) mode. In addition, the L(1) mode is produced as well, perhaps due to the transducers being slightly misaligned with the sample or miscut with respect to the crystal orientation. Unfortunately, considerable transducer ringing is also observed. This may be due to the lack of transducer contact with a rigid frame. The Anopore samples are, of course, extremely light.

The sample length was related to types of modes excited. The sound speed in the

brittle Anopore is high, 3000 m/s for L(1). Therefore, unless the sample is made long enough, the shear and longitudinal pulses overlap. To separate these pulses, the longest possible sample was made although an even longer sample would be preferred.

The transducers were bonded again using Bipax 2101 epoxy and the signal could be checked at room temperature. The sample was fastened to the ultrasonic cell insert supported only by its electrical connections. All the experimentation was done using a piece of Anopore 1.9 centimeters long with 20 MHz shear transducers.

3.2 - Ultrasonic Spectrometer

The experiments are almost exclusively concerned with sound velocity and attenuation changes and hardly at all with the absolute values. Therefore, the ultrasonic spectrometer is designed to measure high-resolution sound velocity and attenuation changes using a phase-sensitive pulse-echo technique. Signals from 3 to 150 MHz can be generated and sound velocity and attenuation changes of 10^{-5} and 0.005 dB respectively can be resolved. Absolute values can be determined within no better than a few percent.

The rationale of the design of ultrasonic spectrometer (Figure 3.2 [37]) along with the overall operation will now be explained. No attempt will be made to discuss every component. In this phase-sensitive technique, the transmitting transducer is excited with a short RF pulse. The received signal is broken into components in-phase and quadrature

Signal Generators

CW Marconi 2022A

LOCAL Marconi 2018

Amplifiers

310 Broadband gated amplifier, Matec 310

254 Broadband pre-amplifier, Matec 254

625 Broadband receiver, Matec 625

A1 Buffer amplifier, Mini-Circuits MAR

A2 +21 dB amplifier, Mini-Circuits ZHL-1A

A4 Buffer amplifier, Mini-Circuits ZHL-1A

A5 pre-amplifier, Mini-Circuits MAR 6

Other Components

Mixer Mini-Circuits ZAD 1

PA Programmable attenuators

BPF 155 MHz Coax band-pass filter, I-tel

LPF 5 MHz low-pass filter, Wavetek AL4BB5

S2 Signal splitter (0°,90°), Mini-Circuits ZSCQ-2-180

Key to Figure 3.2

with a reference signal. Thus, a frequency generator produces a continuous wave of the desired frequency (RF) that is split into two signals, here referred to as RF sample signal and RF reference. The continuous wave RF sample signal is converted into pulses by the gated amplifier. Generally, these pulses are about 5 microseconds long and are produced at a repetition rate of 500 per second. The sound wave arrives at the receiving transducer after transit time t_0 . In addition, some of the sound wave may be reflected at this interface and bounce between sample ends several times. These echoes excite the receiving transducer at times $3t_0$, $5t_0$, and so on.

The size of the pulse sent to the sample can be a concern. Naturally, they should be as large as possible to increase signal to noise ratio. However, dissipation in the sample may cause heating if the amplitude of the sound waves is too large. The pulse size can therefore be adjusted to appropriate levels before reaching the sample using programmable attenuators (sample heating can also be reduced by decreasing the repetition rate).

Sound velocity measurements require that the received pulse be separated into components in-phase and quadrature with the reference. To accomplish this, the sample signal must be split and one part phase shifted 90° . Unfortunately, phase-shifters operate for a narrow band of frequencies and thus only a limited frequency range is possible. Either numerous phase-shifters must be employed or a heterodyne system put in place.

The heterodyne system was constructed using a second frequency generator called the local oscillator (LO). The LO produces a continuous wave at frequency $RF + 155$ MHz that is completely removed from the sample. The LO is split into two signals, one

mixed with the RF sample signal and the other with RF reference. Both signals are now comprised of 155 MHz and $155 \text{ MHz} + 2\text{RF}$ components. The higher frequency component in each is immediately filtered leaving 155 MHz sample signal and reference. Now, with all signals converted to 155 MHz irrespective of RF, only one (155 MHz) phase-shifter is required for velocity measurements.

The 155 MHz sample signal is divided into three components: X, Y, and Z. The X is the sample signal mixed directly with the reference and filtered. The remaining dc offset is the in-phase portion of the signal. The Y is the sample signal first phase shifted 90° and then mixed with the reference and filtered. The remaining dc offset is the quadrature portion of the signal. The Z has no phase sensitivity as it is simply the rectified sample signal.

A typical oscilloscope trace of X and Y is shown in Figure 3.3. The first pulse, called the "main bang", is electromagnetic crosstalk between sending and receiving sides of the spectrometer. The main bang is important only in indicating the arrival of signal at the sample. The next pulse is the result of one way travel of sound through the sample and is the primary source of data. To avoid overlap of the main bang and the first echo, any sample must be made long enough so that its transit time is greater than the pulse width. All subsequent pulses are echoes and, if large enough, can be used for data as well. Once the X, Y, and Z components have been measured, sound velocity and attenuation changes can be easily determined. The phase of the received pulse is simply

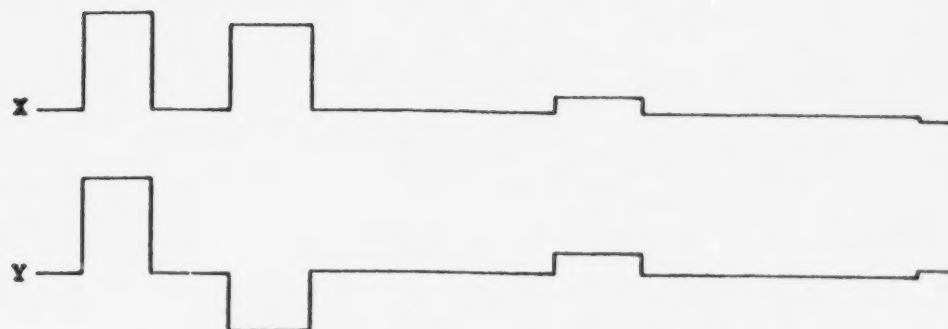


Figure 3.3 - Oscilloscope Trace of X and Y Components
Typical X and Y components show main bang, first, and succeeding echoes.

$$\phi = \tan^{-1} \left(\frac{Y}{X} \right) . \quad 3.1$$

The change in sound velocity is related to the change in the phase by

$$\frac{V}{V_o} = \frac{1}{1 - \frac{\Delta\phi}{2\pi f t_o}} , \quad 3.2$$

where f is the RF frequency and t_o is the initial transit time. Attenuation changes can be calculated from X and Y or Z data:

$$\alpha = \log (Z^2) = \log (X^2 + Y^2) . \quad 3.3$$

Data for all desired frequencies are taken simultaneously during one trip through the temperature vector. That is, at a given temperature, all frequencies are scanned before moving to the next temperature. While equilibrating to the next temperature,

similar data are taken on a 20 dB fixed attenuator. This "drift data" are later subtracted and eliminates long term changes in the spectrometer like drift in amplifier characteristics due to room-temperature changes.

Signal averaging is done over at least 2000 pulses for a single data point. The speed of data acquisition is therefore determined by the repetition rate. Typically 5 frequencies of data and drift takes about 15 minutes. The active baseline is measured before taking data and while taking data. The latter is taken at some time long after any echoes have died out but before the start of the next pulse. Once subtracted from the data, this background eliminates short term drift.

3.3 - Dilution Refrigerator

The cold environment for the experiments was provided by a continuous cycle dilution refrigerator [37]. This refrigerator (Figure 3.4) was preferable to an available helium evaporation cryostat [45] since data below 1 K was needed. With a relatively small throughput of about 1 torr-liter per second, the ultimate temperature of the mixing chamber is 80 mK. This particular dilution refrigerator is also surprisingly efficient on liquid helium consumption. It requires only 5 to 7 liters per day to keep cold.

The ultrasonic cell that holds the sample and insert is situated in the middle of the mixing chamber stage with the fill line thermally anchored to all preceding stages. Ideally, all air and moisture would be removed from the cell before cooling because these

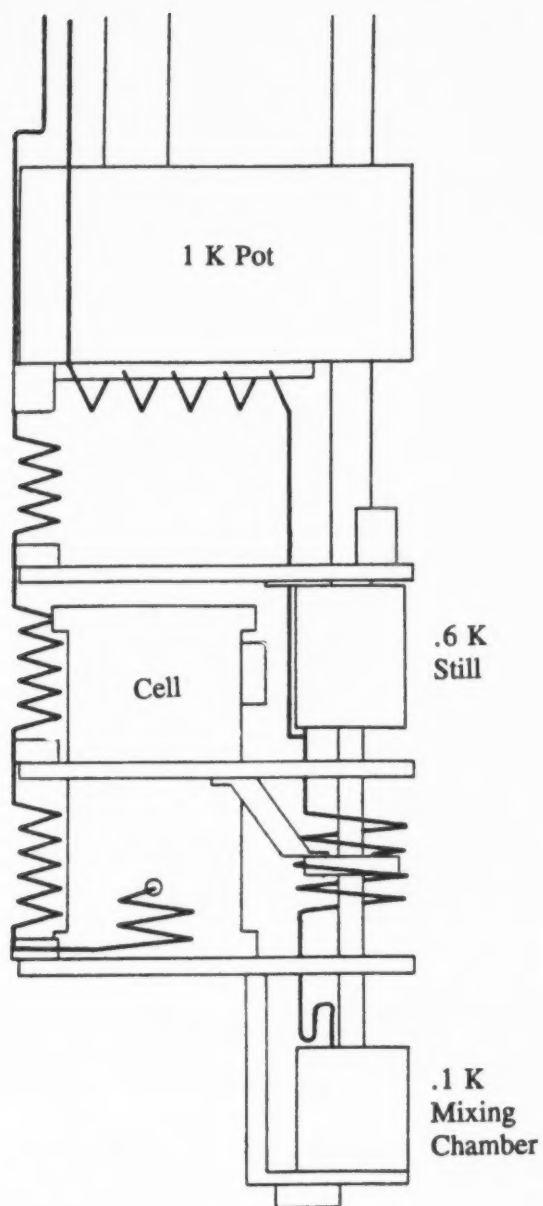


Figure 3.4 - Dilution Refrigerator

The dilution refrigerator can cool to 80 mK and was the cold environment for all experiments in this dissertation (figure taken from Mulders, 1989 [37]).

contaminants will freeze on the surface of the porous material. As an example of this problem, consider Anopore Membranes. Only one torr of air would cover a few monolayers of a typical Anopore sample. However due to the narrow fill line, vapor pressures well below 1 torr in the cell may be difficult to reach. Thus during leak checking, the cell is evacuated about 15 minutes, pressurized to 500 psi with helium, and checked from the outside. This process is repeated several times, flushing unwanted air that cannot be pumped out.

A typical cooldown is a day long process. All joints and seals on the can, pot, refrigerator, and cell must be leak checked. Assuming no leaks exist, helium exchange gas is admitted into the vacuum space inside the can. The dilution refrigerator is then precooled in liquid nitrogen, saving considerable liquid helium. Usually 60 liters of liquid helium will cool the dilution refrigerator to 4.2 K and fill the dewar to operational levels. Once cold, the can is evacuated and the pot filled. After the pot reaches about 1 K, the $\text{He}^3\text{-He}^4$ mixture is circulated and the mixing chamber cools.

Precise temperature control is attempted only on the mixing chamber where a calibrated germanium thermometer and 150 ohm heater are fastened. The temperature is determined via a four terminal resistance reading by a Quantum Design (1802) R/G Bridge. The amount of heat supplied by a driver on the bridge is determined by two constants: the gain and integrator. The gain is simply a value that is multiplied by the temperature difference to determine the heat output. The integrator is a time constant that adds or subtracts heat proportionally to the inverse relaxation rate. The total heat output is the sum of these two signals. Temperature control to within 0.1% of the

absolute temperature is generally acceptable.

The cell has considerable volume not taken up by the sample and insert. This volume, about 10-15 cc, is orders of magnitude larger than the void volume of the sample. Since helium freezes at pressures well in excess of the vapor curve, the sample must initially be surrounded by bulk liquid at high pressure.

The cell is filled and pressurized with liquid helium at 4.2 K via an external gas handling system, high purity helium tank, and pressure gauge. The pressure gauge, Setra Systems Model 206/207, is linear to within 0.1% from 0 to 5000 psi. It is accurate to within 0.13% and reproducible to within 0.08%. The high reproducibility is necessary when studying the freezing curve minimum of helium in porous media where pressure changes of a few parts per thousand drastically affect the temperature of solidification.

Cooling the fridge begins by filling and pumping on the pot. Once the pot is cooled, the cell fill line plugs immediately leaving a constant amount of helium in the cell. Thus, experiments are performed under constant density (isopycnal) conditions in the cell. As the cell temperature is reduced, the bulk helium freezes and the cell pressure drops considerably. The temperature and pressure of the onset and completion of bulk freezing can be predicted since the density of liquid and solid along the bulk melting curve are known. At some finite temperature below the completion of bulk solidification, freezing in the pores starts. The surrounding bulk then acts as a helium reservoir as solid is drawn into the pores during freezing. The cell pressure drops during this process.

The considerable bulk helium proves to be both advantageous and problematic.

The helium, liquid or solid, increases the heat capacity and therefore the thermal time constant of the mixing chamber stage dramatically. Thus, with the cell full, the temperature can be raised and lowered basically monotonically by using an appropriate gain and no integrator. During bulk freezing, however, the large latent heat and small cooling power associated with conduction from the pot can halt cooling for days. The $\text{He}^3\text{-He}^4$ mixture must be circulated during bulk freezing as opposed to simply allowing it to condense in to achieve reasonable cooling times.

Two small modifications were made on the dilution refrigerator and are worth noting. First, the section of coaxial cable connecting the 4.2 K bath to the 1 K pot was changed from copper to stainless steel. The heat load on the pot was halved and time between fillings doubled from one to two days. This is extremely important because an entire scan could now be completed in this period thereby ensuring isopycnal conditions throughout. The tradeoff was an ultrasonic signal a few dB smaller due to the higher resistance cables. Second, a 150 ohm heater was fastened to the pot. Thus, after a run was completed, the pot could be emptied and the cell repressurized in minutes instead of hours.

CHAPTER 4 - FINITE-SIZED SYSTEMS

Freezing and superfluidity of helium in small or reduced dimensions can be markedly different than in bulk and Chapter 4 is an overview of the effect of finite-size on these transitions. On the most fundamental definition of a transition, however, superfluidity and freezing are dissimilar. A transition of 1st order is defined as having discontinuous 1st derivative of the Gibbs free energy between the two phases. Freezing is a true 1st order transition, with discontinuous entropy and molar volume between the two phases. Meanwhile, the superfluid transition has no such discontinuities and cannot be classified as 1st order. Instead, superfluidity is a continuous transition with a singularity in the heat capacity at the critical temperature. Therefore, Chapter 4 is divided into two sections. Sections 4.1 and 4.2 are separate discussions of the effect of confinement on freezing and superfluidity of helium, respectively.

4.1 - Freezing and Melting

Recall that the liquid helium in pores can be divided into two components. The first is the dense solid-like layer of one or two atomic thicknesses that contacts the pore wall. Strong van der Waals attraction with the amorphous glass (and perhaps aluminum oxide) make this solid film highly disordered. Meanwhile, the rest of the contained helium acts nearly like bulk fluid, not significantly influenced by the glass and with nearly bulk density.

This disordered layer may be the mechanism for the undercooling of liquids in pores. It has been demonstrated that the liquid not the solid phase of helium preferentially wets the surface of some substrates including glass [46]. That is, $\sigma_{lg} > \sigma_{sg}$, where these are the solid-glass and liquid-glass interfacial energies. The interfacial energy between the solid phase of helium and glass may be unusually large due to the obvious mismatch between an ordered solid and the irregular and highly compressed helium monolayer. Crystallites should then form with as little contact with the pore wall as possible. This spontaneous solid formation without benefit of contact with surfaces or impurities is called homogenous nucleation. In the Gibbs-Thomson model of homogeneous nucleation [47], the equilibrium state is determined by surface and volume free energies. Assuming the solid nucleates as a sphere of radius r , the change in Gibbs free energy is expressed as

$$\Delta G = 4\pi r^2 \sigma_{l-s} - \frac{4}{3}\pi r^3 \frac{(g_l - g_s)}{v_s}, \quad 4.1$$

where σ_{l-s} is the liquid-solid interfacial energy, g_l and g_s are the molar free energies of the respective liquid and solid phases, and v_s is the molar volume of the solid. In porous media, the size of solid nuclei is restricted to the pore diameter or smaller. The surface free energy, negligible in large, bulk systems, makes a significant contribution to the total free energy of such a pore-sized droplet.

The change in molar free energies can be expressed as an expansion in ΔT , the amount of undercooling below the bulk freezing temperature (T_B):

$$g_l - g_s = \left(\frac{\partial(g_l - g_s)}{\partial T} \right)_P \Delta T + \frac{1}{2} \left(\frac{\partial^2(g_l - g_s)}{\partial T^2} \right)_P (\Delta T)^2 + \dots \quad 4.2$$

Simplifying the partial derivatives to thermodynamic quantities yields

$$g_l - g_s = \frac{l_v}{T_B} \Delta T + \frac{1}{2} \frac{(c_l - c_s)}{T_B} (\Delta T)^2 + \dots, \quad 4.3$$

where l_v is the molar latent heat and c_l and c_s are the liquid and solid molar heat capacities, respectively. Small undercooling is assumed so only the quantity to first order in ΔT will be kept for further calculations so that free energy change becomes

$$\Delta G = 4\pi r^2 \sigma_{l-s} - \frac{4}{3}\pi r^3 \frac{l_v \Delta T}{T_B} . \quad 4.4$$

The behavior of the Gibbs free energy change is shown in Figure 4.1 and is interpreted for freezing in pores as follows. Nuclei of various radii are continually forming via fluctuations. In large, bulk systems, nuclei with radii that overcome the energy barrier (r_B) continue to grow. However, in small pores, nuclei can form and grow no larger than a pore size. For a given undercooling, a pore-sized droplet may have overcome the barrier but still have a positive free energy change as it is restricted from growing any further. Similar fluctuations should drive it back into the liquid state. A critical radius (r_c) for freezing in pores is then defined as one having a negative free energy change (where the curve crosses zero):

$$r_c = \frac{3\sigma_{l-s}v_s T_B}{l_v \Delta T} . \quad 4.5$$

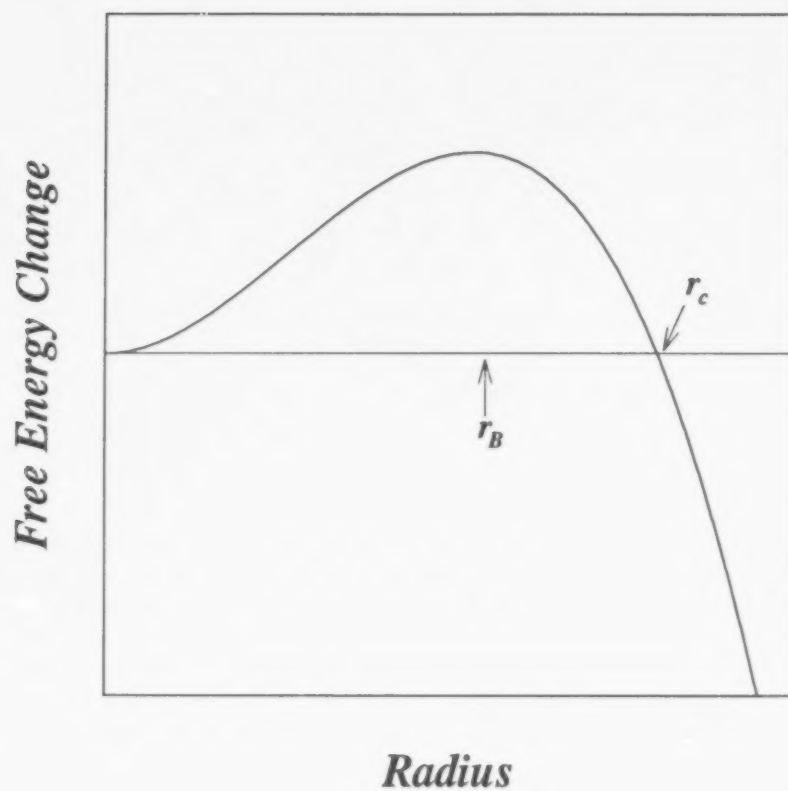


Figure 4.1 - Gibbs Free Energy Change of Nucleating Sphere
The Gibbs free energy change for a nucleating sphere has a critical radius (r_c) for stable formation of solid in pores.

Stable solidification presumably occurs when the critical radius equals the pore size (d_p).

Therefore, the freezing point depression can be predicted for a given pore size (d_p):

$$\Delta T = \frac{3\sigma_{l-s}T_B}{l_v d_p} . \quad 4.6$$

In the case of helium, it is more appropriate to express freezing in pores in terms of elevated pressures as opposed to depressed temperatures since there are pressures where bulk freezing ends at some finite temperature but the helium in the pores remains liquid at 0 K. This is accomplished by expressing molar free energies as an expansion in ΔP at constant temperature. That is,

$$g_l - g_s = (v_l - v_s)\Delta P . \quad 4.7$$

Thus, using the previous arguments, solidification in pores (d_p) requires a pressure increase of

$$\Delta P = \frac{3\sigma_{l-s}v_s}{d_p(v_l - v_s)} . \quad 4.8$$

Calculations of the excess pressure required to solidify helium in media with a known pore size is limited by the predictability of the liquid-solid interfacial energy (σ_{ls}). Bulk values are 0.084 erg/cm² for the bcc solid and 0.16 erg/cm² for the hcp solid [48]. However, neither value may be applicable since crystalline order appears to be suppressed for solids in pores, particularly those with low freezing temperatures. Also, the radius of curvature of a nucleate may be only tens of angstroms. The interfacial energy may be sensitive to the radius of curvature at these sizes. Finally, the solid phase may initially wet the pore wall slightly. In that case, these interfaces should be considered as well in the Gibbs-Thomson model.

Freezing should continue with reduced temperature into smaller regions both as growth of the solid droplets or as homogenous nucleation when smaller nuclei become stable. This explains the broad transition where liquid and solid coexist over a finite temperature range.

When warmed, considerable hysteresis is observed between freezing and melting. Figure 4.2 is superimposed sound attenuation data of argon-filled Vycor [2] for a group of hysteresis loops. Each loop begins with only liquid in the pores and is cooled past T_f so that freezing has initiated. For Curve A, cooling is halted at 68 K, presumably after all argon in the pores has frozen. All subsequent curves have increasingly high reversal temperatures where a fraction of the adsorbed argon is still liquid. Curve F is warmed only about 50 mK below T_f . Like freezing, the melting process appears to occur over a finite temperature range. For each hysteresis loop, melting is complete near 80 K, about halfway between bulk freezing and T_f and independent of the reversal temperature.

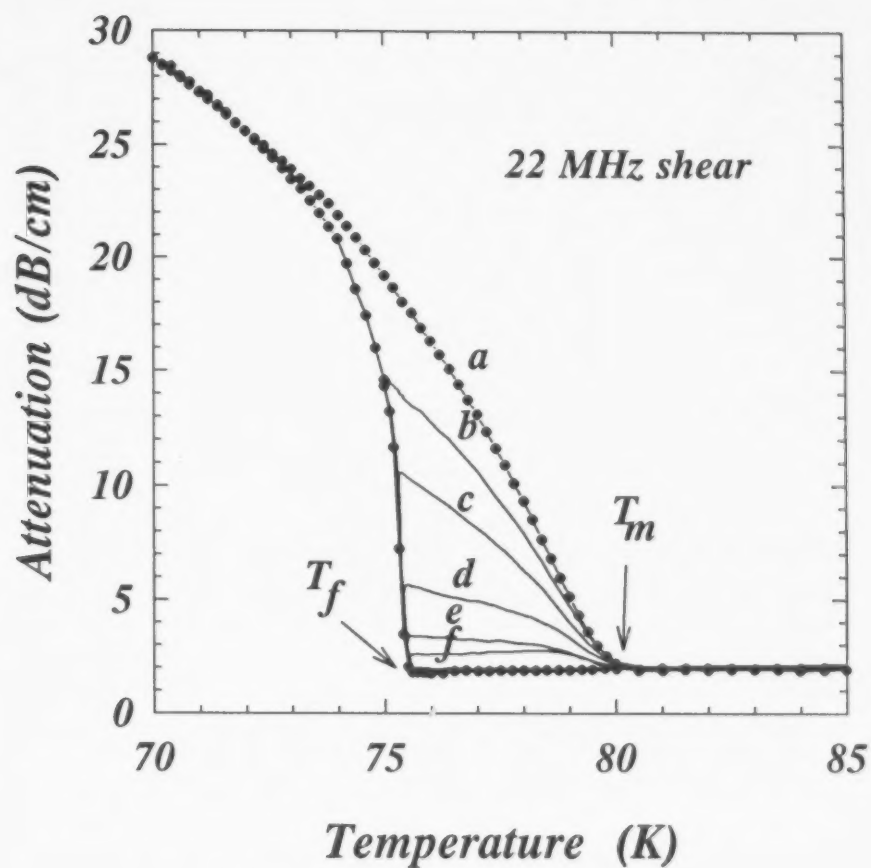


Figure 4.2 - Ultrasound Attenuation in Argon-Filled Vycor

Curves A-F are hysteresis loops for argon-filled Vycor that are cooled progressively smaller amounts below T_f . The melting temperature (T_m) is the same for each loop. However, most of melting in the lower curves occurs just below T_m (figure taken from Molz et al, 1993 [2]).

Some features of the hysteresis depend on reversal temperatures. At high frozen fractions, melting seems to start immediately when warmed as the sound attenuation decreases rapidly. When the temperature is reversed just below the onset of freezing, where presumably little solid exists, melting appears to be suppressed until just below T_m as the attenuation remains nearly constant until just below T_m . This may be consistent with the Gibbs-Thomson model, with the largest pores freezing first and melting last.

Some mechanisms for the observed hysteresis have been suggested. These include simple geometrical arguments and pictures involving changes in the interfacial energies to more complicated mechanisms involving the Gibbs free energy during heterogeneous nucleation [31]. In all cases, however, the hysteresis between freezing and melting in small pores must be the result of the solid phase becoming more energetically stable after formation.

A simple model to describe the hysteresis involves the growth of droplets into the smaller bottlenecks. Consider solidification in a Vycor-like system of cylindrical pores interconnected by narrow channels. The solid nucleates in the largest pores, presumably as a sphere. The solid must obviously grow from the sides into the cylindrical-shaped pores eventually into the more restricted channels. The freezing and melting of solid should be reversible at this stage. However, some solid must eventually connect with solid from a neighboring pore. Now, instead of having two liquid-solid interfaces, there is one grain boundary where two different crystal orientations meet. If the liquid-solid interfacial energy of twice the surface area that has joined is greater than that of the grain boundary that has formed, as has been suggested [49], the solid phase becomes more

stable. Clearly, this should result in higher melting temperatures. For a range of void sizes, the largest combinations pores and channels have the highest freezing and melting temperatures. Thus, it is expected that hysteresis should occur with the melting temperature independent of the amount initially frozen. Clearly, this closely describes some of the features of the hysteresis loop. Notice this model requires an interconnected network of pores unlike those in Anopore Membranes.

Another possible interpretation [49] of the hysteresis involves the amorphous monolayers against the pore walls. When the pores become filled with solid, the disordered nature gradually becomes more crystalline away from the wall. In time, the amorphous monolayers may rearrange and gain the order of the solid. This annealing process may lower the solid-glass interfacial energy and make the solid phase stable to higher temperatures. In addition, more of melting may occur gradually at the pore wall instead of spontaneously from the middle.

An essential difference between these two models is that the first requires interconnected pores with a distribution of sizes for significant hysteresis. Uniform, noninterconnected pores may melt at nearly the same temperature as freezing under this interpretation. Thus, the freezing and melting process in Anopore Membranes may offer considerable insight into the hysteresis.

4.2 - Superfluidity

Superfluidity of helium in Vycor, aerogels, and xerogels has features markedly different than in bulk. Heat capacity, torsional oscillator, and fourth sound experiments [23,24] studied the behavior of helium in small pores. The onset of superfluidity in small pores is suppressed to lower temperatures and is quite sharp despite the often complicated nature of the pore geometry. The lambda point in pores is suppressed a few hundredths of a degree in highly porous silica aerogels and as much as 0.23 K in Vycor. The critical exponent with which the superfluid fraction disappears in Vycor is nearly the same as in bulk (.67). However, values in 94% porous silica aerogel and 60% porous xerogel are 0.81 and 0.89, significantly higher than that of bulk and suggest that the transition belongs to another universality class. Singularities in the heat capacity at the lambda point of bulk are not present for helium in Vycor but have been observed for helium in silica aerogel.

No attempt to explain these features will be made as that is not within the scope of this dissertation. Still, a qualitative picture of the lambda point suppression will be presented. This model [50-51], from Ginzburg-Pitaeski theory, predicts the lambda point suppression in porous media but explains none of the other aforementioned critical behavior. To appreciate the Ginzburg-Pitaeski model, the concept of the "condensate wavefunction" in superfluid helium must be made clear.

A qualitative picture of the normal fluid to superfluid transition in helium involves the distribution of energy states. Above the critical temperature (T_λ), most helium atoms

occupy excited states. However, below T_λ , a macroscopically large number of helium atoms condense into the lowest energy state. This fraction of ground state atoms is called the condensate and presumably corresponds to the superfluid fraction. For convenience, He I designates the normal state helium above the critical temperature while the combination of normal state and condensate below T_λ is He II.

This continuous change to a highly ordered state is described by an order parameter that, like the superfluid fraction itself, is zero at or above T_λ and slowly increases to unity at $T = 0$ K. Thus, a sensible order parameter for the superfluid transition is the condensate wavefunction (Ψ_s). The condensate wavefunction governs the entire superfluid motion and the superfluid density (ρ_s) at any temperature is expressed as

$$\rho_s = m_4 |\Psi_s|^2 . \quad 4.9$$

The form of the condensate wavefunction is generally

$$\Psi_s(r) = \Psi_0 e^{iS(r)} , \quad 4.10$$

where the phase, $S(r)$, is a slowly varying function of position and is coherent for the entire superfluid fraction. With this function, the velocity of the superfluid is proportional to the gradient of the phase. The condensate wavefunction has a characteristic scale called the coherence length. The coherence length, $\xi(T)$, represents the distance required for the wavefunction to change appreciably. It diverges at the bulk lambda temperature and decreases to a few angstroms at absolute zero. Since the condensate wavefunction must disappear at any wall or boundary, the existence of superfluidity at a given temperature has an apparent size constraint. For a system where the smallest dimension is significantly less the coherence length, no nontrivial condensate wavefunction is possible and superfluidity cannot exist.

The formalism of this restriction is provided from Ginzburg-Pitaevskii theory. In accordance with Landau theory of second-order phase transitions, the GP free energy density of He II (g_{II}) can be written as an expansion of the order parameter near the critical temperature but is modified to include a kinetic energy term. That is,

$$g(r)_{II} = g_I + \alpha |\psi(r)|^2 + \frac{\beta}{2} |\psi(r)|^4 + \frac{\hbar^2}{2m} |\nabla\psi(r)|^2, \quad 4.11$$

where the coefficients are assumed to be powers of $(T-T_\lambda)$. Generally, $\alpha(T) = -A(T-T_\lambda)$ and $\beta(T) = \beta$ are accepted choices. Since equilibrium conditions apply for g_{II} at any temperature, this expression must be minimized with respect to either Ψ or Ψ^* using the

Euler-Lagrange equation. This yields

$$\nabla^2 \psi + \frac{2m_4 A(T-T_\lambda)}{\hbar^2} \psi - \frac{2m_4 \beta}{\hbar^2} |\psi|^2 \psi = 0 . \quad 4.12$$

Now, the coherence length $\xi(T)$ is introduced and defines a minimum scale for appreciable variation of the condensate wavefunction. Its form is $\xi(T) = [\hbar^2/2m_4 A(T-T_\lambda)]^{1/2}$. Ignoring the final term, equation 4.12 reduces to

$$\nabla^2 \psi - \frac{1}{\xi^2(T)} \psi = 0 . \quad 4.13$$

with the boundary conditions that Ψ vanishes at the pore walls ($x = 0, d_p$). Clearly, for a porous media such that $d_p < \pi \xi(T)$, there is no solution except $\Psi = 0$ and thus superfluidity is quenched. Only when the coherence length becomes as small as the pore can superfluidity occur. This qualitative argument predicts reduction of the lambda transition in small pores, with the reduction scaling to the inverse square root of the pore size, $(T_\lambda - T) \propto d_p^{-1/2}$. The suppression in the lambda point in Vycor-sized pores can be calculated from the value of the bulk coherence length: $\xi(T) \approx 4 \times 10^{-10} (T_\lambda - T)^{-1/2} \text{m}$. Using 40 Å for d_p yields a suppression of about 0.1 K, comparable to the measured 0.23

K suppression.

CHAPTER 5 - RESULTS

Chapter 5 is a presentation and analysis of the helium data for Vycor, silica aerogel, and Anopore Membranes. Since this takes substantial space including figures, Chapter 5 is divided into separate sections on Vycor, silica aerogel, and Anopore.

Some statements about the data should be mentioned. All pressures quoted for any individual scan refer to the pressure at the completion of bulk freezing. Since there is hysteresis between freezing and melting in small pores, there should be two curves: one for freezing and one for melting. To eliminate any ambiguity, helium in pores solidifies on the "freezing curve" and melts on the "melting curve". The phase diagrams for helium in these porous materials will be presented at the end of the sections.

Generally, attenuation data are presented as absolute changes as opposed to attenuation changes per unit length or per frequency (damping). Sound velocity is

presented as dimensionless relative changes as opposed to percent. When presented together, the sound velocity and attenuation symbols are triangles and circles, respectively, with solid symbols for cooling and hollow symbols for warming.

Since helium in small pores freezes at pressure above that of bulk (Figure 5.0.1), the cell is filled at 4.2 K and pressure well in excess of the minimum pressure for bulk freezing at 0 K (point A). During cooling, the pressure in the cell drops in accordance with helium expansion and compressibility. At point B with the same initial density, the bulk melting curve is reached. While on the bulk melting curve the pressure in the cell drops substantially. At point C all the helium surrounding the sample has frozen while the confined helium remains liquid. Clearly the point where all bulk has solidified is important and can hopefully be identified. The liquid in the pores then undercools until point D where freezing in the pores starts. The pressure at which bulk freezing is complete determines the position of the transition in Vycor. At high enough initial pressure, the Vycor melting curve will be met and solidification in pores occurs. However, for certain starting pressure at 4.2 K (point E) no freezing happens in the pores although all the surrounding bulk has solidified. In this case, bulk freezing starts (point F) and does complete (point G). The pressure at the completion of bulk freezing is below the Vycor freezing curve. On cooling, the Vycor lambda line is crossed (point H) and only superfluidity in the pores is observed. There also appears to be a pressure range where first the Vycor lambda line and then the Vycor freezing curve are reached. That is, both transitions can happen on the same scan. All three situations will be explored. Similar behavior is expected for silica aerogel and Anopore.

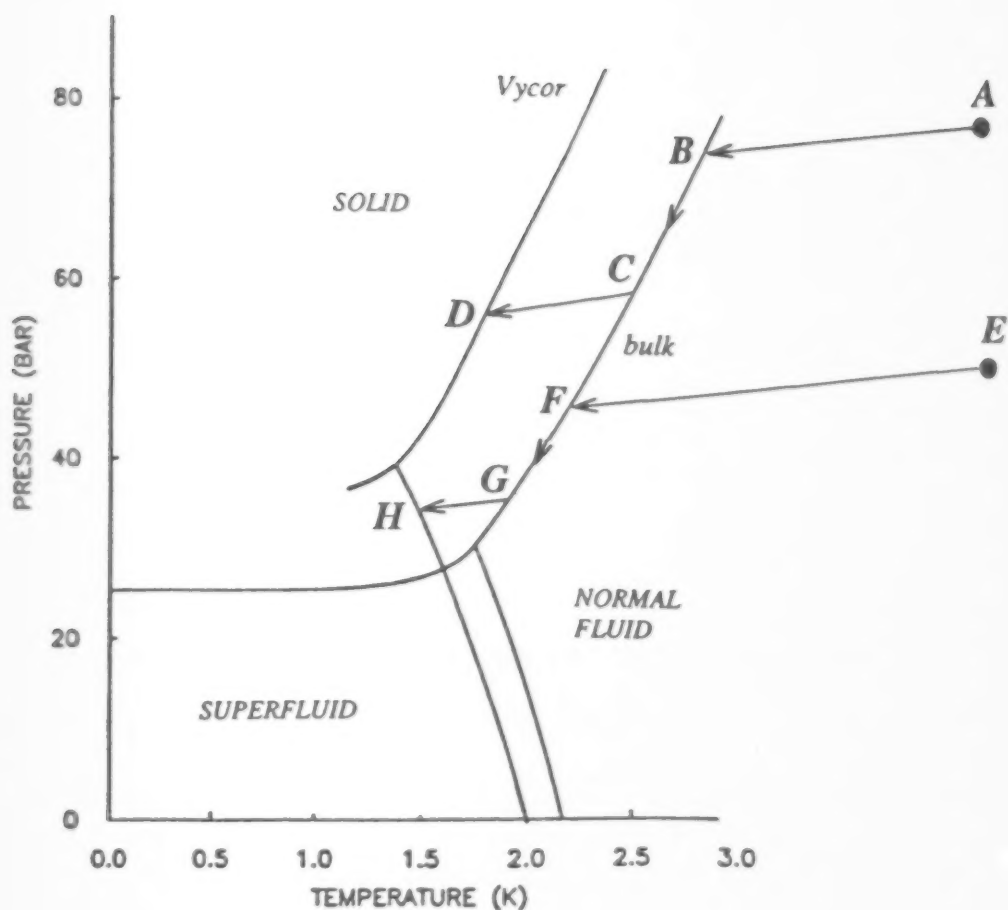


Figure 5.0.1 - Cell Pressure-Temperature Curve

Path A-D is a typical cell temperature-pressure curve for freezing of bulk helium followed by freezing of helium in the Vycor. Path E-H is a typical temperature-pressure curve for freezing of bulk followed by superfluidity of helium in Vycor.

5.1 - Helium in Vycor

All helium in Vycor data were taken on a 1.37 centimeter sample with 28 MHz LiNbO_3 shear transducers. Every indication is that the pulse produced is shear with no overlapping longitudinal component. Based on the phase diagram for helium in Vycor the transitions that should occur are highly dependent on the filling pressure. Thus scans were done with a variety of initial filling pressures near and greatly in excess of the minimum pressure required for helium to solidify in Vycor.

The highest filling pressure at 4.2 K was about 120 bar. Bulk freezing for this filling started near 3.80 K. Sound velocity (triangles) and attenuation (circles) at 93 MHz and below 3.50 K are displayed in Figure 5.1.1. The scan has clearly been started during bulk freezing, where the pressure drops considerably with temperature. Liquid helium density in the pores decreases in response to this pressure change so that the sound velocity increases rapidly. Bulk freezing is complete at 3.03 K (T_B), which corresponds to 81.6 bar, at which point the Vycor is filled with liquid and surrounded by solid. As the scan continues, the liquid in the pores undercools. At 2.35 K, after undercooling 0.68 K, both the sound velocity and attenuation rise sharply indicating that freezing in the pores has begun (T_F). The modulus increase for solid helium overcomes the mild density increase. Upon further cooling, the sound velocity continues to rise until 0.5 K where the relaxation peak associated with TLS occurs. Unlike the start of freezing in the pores (T_F), no sudden change in the sound velocity is present that signals the completion of freezing in the pores. Meanwhile, the attenuation peaks around

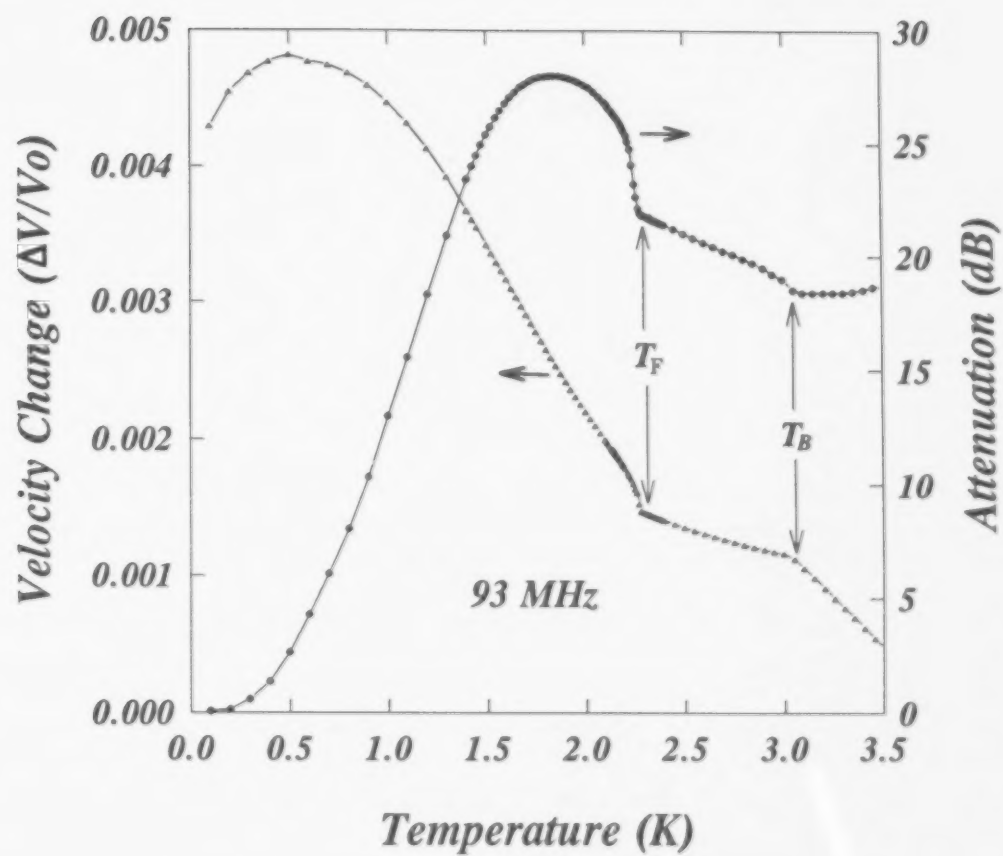


Figure 5.1.1 - Freezing of Helium in Vycor

Sound velocity and attenuation cooling curves at 93 MHz show freezing in Vycor occurs below bulk freezing.

1.84 K where about half of the total velocity change has occurred.

Sound velocity and attenuation for warming are included in Figure 5.1.2. The warming curves (hollow circles and triangles) trace the cooling curves until about 2.0 K where the hysteresis begins. The curves rejoin at 2.7 K, about halfway between T_F and T_B . This point, labeled T_M , is the completion of melting.

The continuous sound velocity increase and the attenuation peaks at temperatures well below T_F could be explained by assuming that not all the helium in the pores freezes. If solidification occurs gradually to the lowest temperatures, the sound velocity should steadily increase. The attenuation peak could indicate a relaxation "squirting" process where liquid moves around solid regions in response to the stress of the sound wave. Further, the point where the hysteresis starts may indicate where a significant number of pores block completely, so that solidification in Vycor takes place at constant density instead of pressure.

However, the cause of the continuous increase in sound velocity and the attenuation peak has been identified as stress relaxation via vacancy diffusion [2,9]. The random orientation of the pore structure with respect to the passing sound wave can cause large local stresses on the pore. The solid helium in the pores can deform through vacancy motion in response to this stress. On a pore-sized scale, relaxation times (τ) for vacancy diffusion are on the order of microseconds. Attenuation peaks occur where $\omega\tau = 1$, where ω is the angular frequency. As shown in Figure 5.1.3, the peak temperatures also increase with frequency, consistent with a thermally activated process. Further, the stiffness of the confined solid helium should be smaller than bulk until the

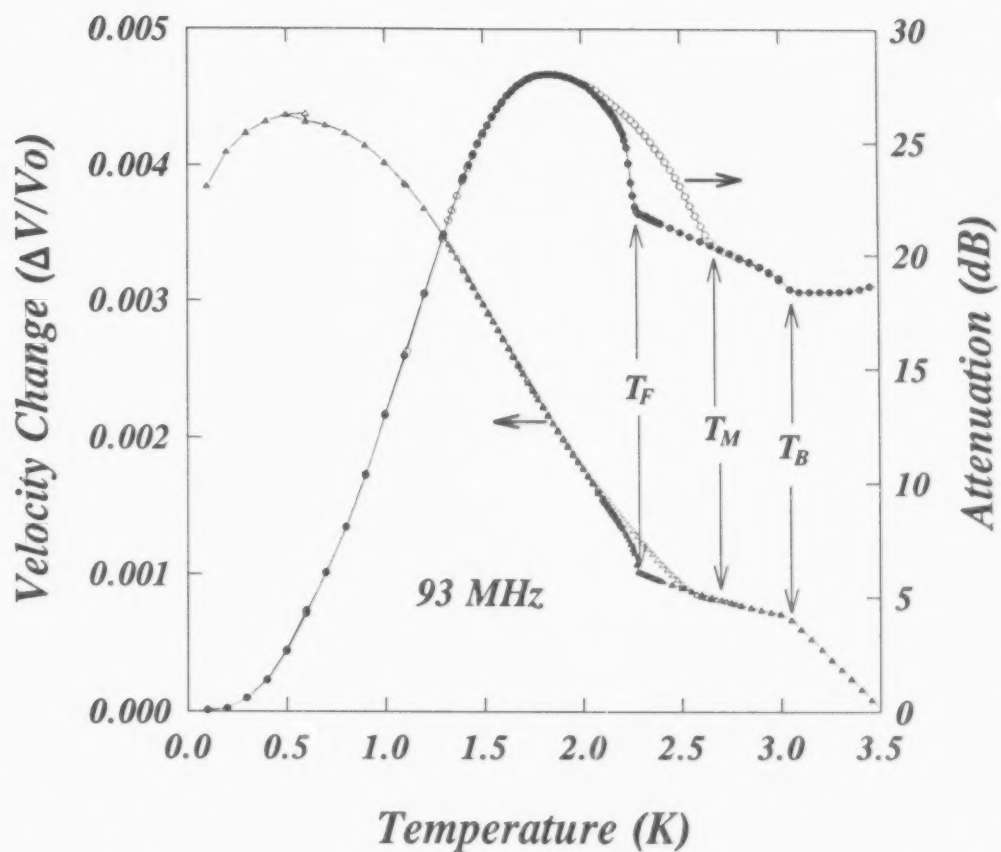


Figure 5.1.2 - Freezing and Melting of Helium in Vycor
 Sound Velocity and attenuation at 93 MHz shows hysteresis between freezing and melting with melting complete below bulk freezing.

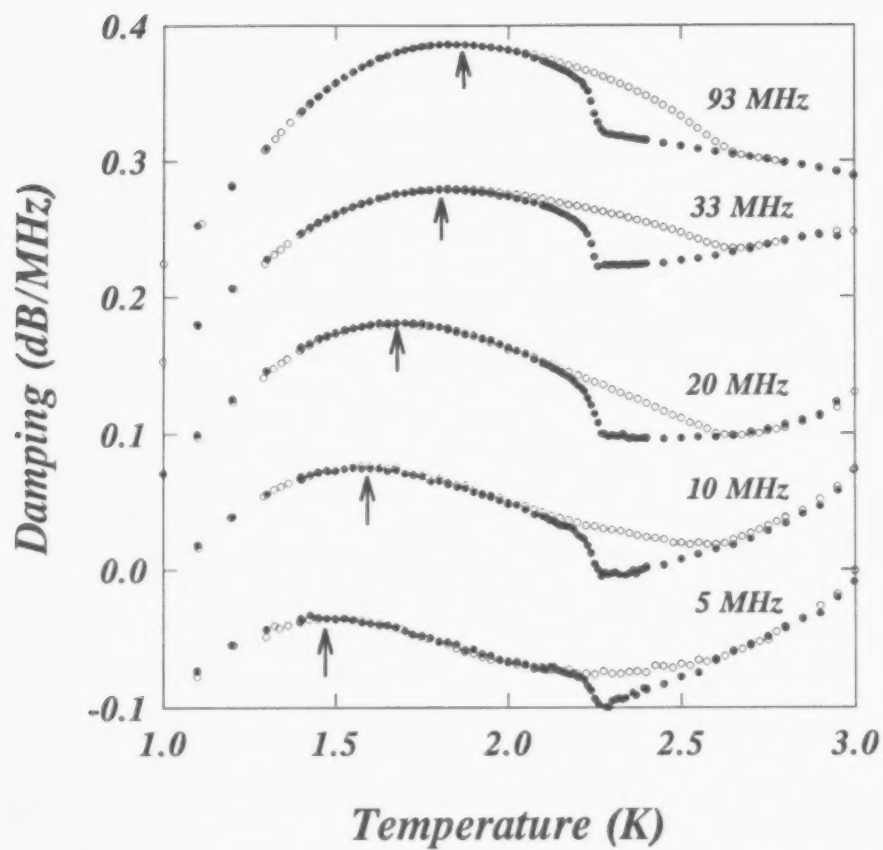


Figure 5.1.3 - Attenuation Peaks of Helium in Vycor

Attenuation shows frequency dependence of peaks temperatures due to thermally-activated vacancy diffusion.

vacancy diffusion becomes frozen out. Thus, the expected sound velocity change is not realized until the lowest temperatures.

The form of the characteristic relaxation time (τ) [52] of a crystal of size L is

$$\tau = \frac{k_B T L^2}{2\alpha \mu V D_0} e^{E_v/k_B T}, \quad 5.1$$

where μ is the shear modulus, α is a shape-dependent numerical factor, D_0 is a diffusion coefficient, V is the volume of a vacancy (essentially the atomic volume in helium), and E_v is the activation energy of mobile vacancies. Given that the attenuation peaks occur at $\omega\tau = 1$, equation 5.1 becomes

$$\omega T_{\max} = \left(\frac{\alpha \mu V D_0}{k_B L^2} \right) e^{-E_v/k_B T_{\max}}, \quad 5.2$$

where $T_{\max}$ is the peak temperature. The activation energy for mobile vacancies can be extracted by a plot of the natural log of $\omega T_{\max}$ versus the inverse peak temperature. Figure 5.1.4 shows such plots for 81.6 (A), 55.8 (B), and 43.6 (C) bar using 93, 33, 20, 10, and 5 MHz waves. The activation energies are 21.9 K, 17.7 K, and 13.6 K,

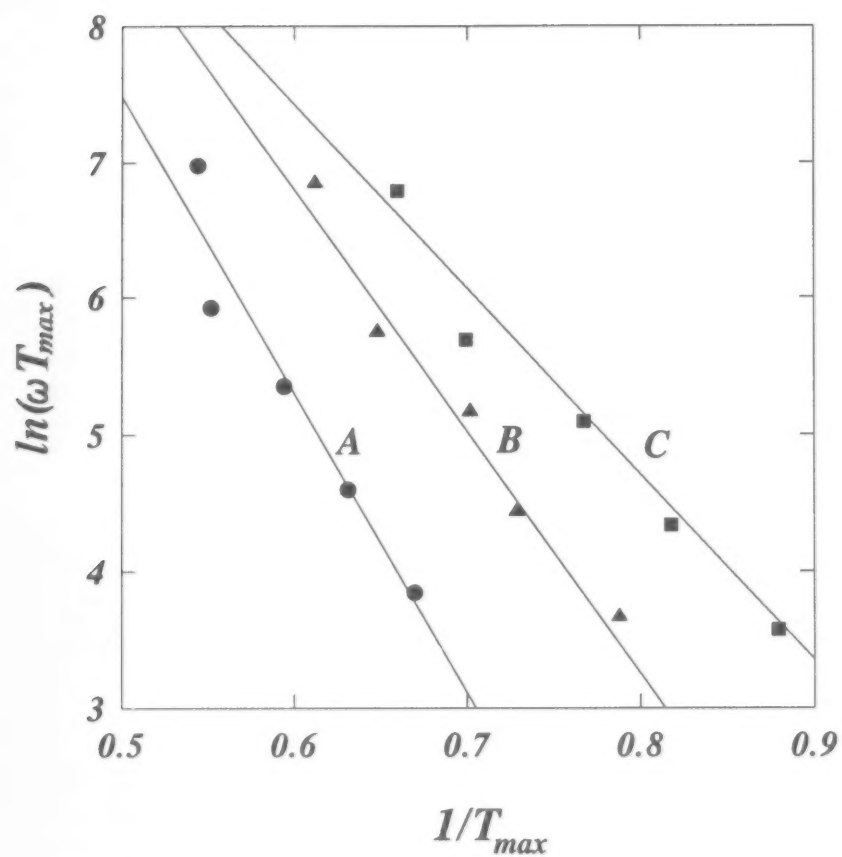


Figure 5.1.4 - Plot of Attenuation Peaks

The plots of $\ln(\omega T_{max})$ versus $1/T_{max}$ at 81.6 (A), 55.8 (B), and 43.6 bar (C) yield activation energies of 21.9 K, 17.7 K, and 13.6 K, respectively.

respectively. Previous measurements [53-54] of diffusion rates of impurities in solid He^4 can be compared. The measured activation energies for He^3 and ion diffusion in He^4 ranged from about 10 K to 40 K over the pressure range with considerable scatter. In addition, like these results, the activation energy increased monotonically with pressure.

Mobile vacancies also have important experimental ramifications [9]. The relaxation time for pressure equilibrium via vacancy diffusion between a Vycor-sized sample and the surrounding bulk helium is about 10 minutes. Since a single data point for the experiments takes at least that long, pressure equilibrium should be maintained. Further, the prior pressure experiments [11] done on helium-filled Vycor powders should also be in equilibrium making the interpretations thereof plausible.

Figure 5.1.5 is an enlargement of the hysteresis region. A few things about the behavior of the hysteresis are worth discussing. First, although the kinks indicating the start of freezing (T_F) and the end of melting (T_M) are very sharp, there are no kinks to indicate where melting begins or where freezing ends. This may suggest that the distribution of smallest pore and bottleneck sizes may be broad while the largest pore sizes have an abrupt upper limit. Although the onset of hysteresis on warming may signal one or both of these points, to comment on the liquid-solid distribution in the pores at lowest temperatures requires data at the Vycor freezing curve minimum.

Second, notice that the sound velocity on warming dips slightly under that during cooling just below T_M even though, at those temperatures, no solid is present on cooling. Apparently, at high enough temperatures, vacancy motion reduces the modulus contribution of solidification to the sound velocity to less than the density contribution.

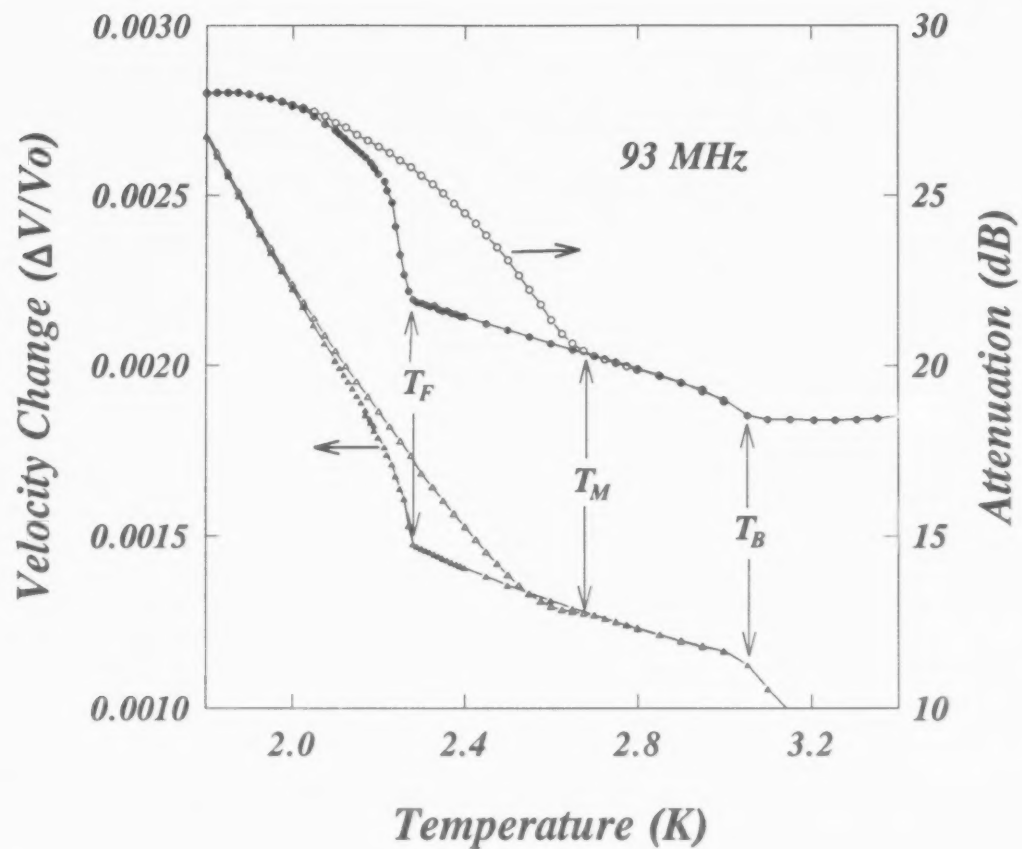


Figure 5.1.5 - Enlargement of the Hysteresis Region in Vycor
 An enlargement of the hysteresis region shows sharp freezing and melting points in Vycor with melting about halfway between freezing in pores and bulk.

The frequency-dependence of this effect can be seen in Figure 5.1.6. For the 81.6 bar scan, 10 MHz and 93 MHz data are displayed. The transition, T_F , is much sharper and the total velocity change by 1.80 K is clearly greater for 93 MHz. On warming, the dip in the sound velocity is more pronounced at 10 MHz although the melting temperature, T_M , is the same. Basically, the solid helium responds more stiffly for higher frequency stress waves. This is not unexpected given vacancy motion where a shorter sound period allows the solid helium less time to relax.

Lower initial filling pressures were used to observe superfluidity in Vycor. Figure 5.1.7 displays sound velocity and attenuation at 93 MHz with an initial pressure slightly below the bulk melting curve minimum where no freezing in pores or bulk can occur. During cooling the mild change in the slope of the velocity curve at about 2.05 K probably indicates reaching the bulk lambda line. Near 1.80 K, the sound velocity increases as the Vycor lambda line is met and superfluid helium decouples. The velocity change by 1.0 K, where nearly all confined helium is superfluid, is about 0.002, comparable to the velocity change due to freezing in the pores. Meanwhile, the onset of superfluidity in Vycor is accompanied by a 2 dB critical peak in attenuation. The 0.25 K depression of superfluidity from bulk to Vycor is about the same as at saturated vapor pressure as the lambda lines are parallel. Sparse warming data are superimposed but indistinguishable from the cooling data demonstrating that superfluidity in pores is completely reversible.

Based on the phase diagram, there should be a starting pressure so that both the Vycor lambda line and then melting curve are crossed. Clearly, this pressure is between

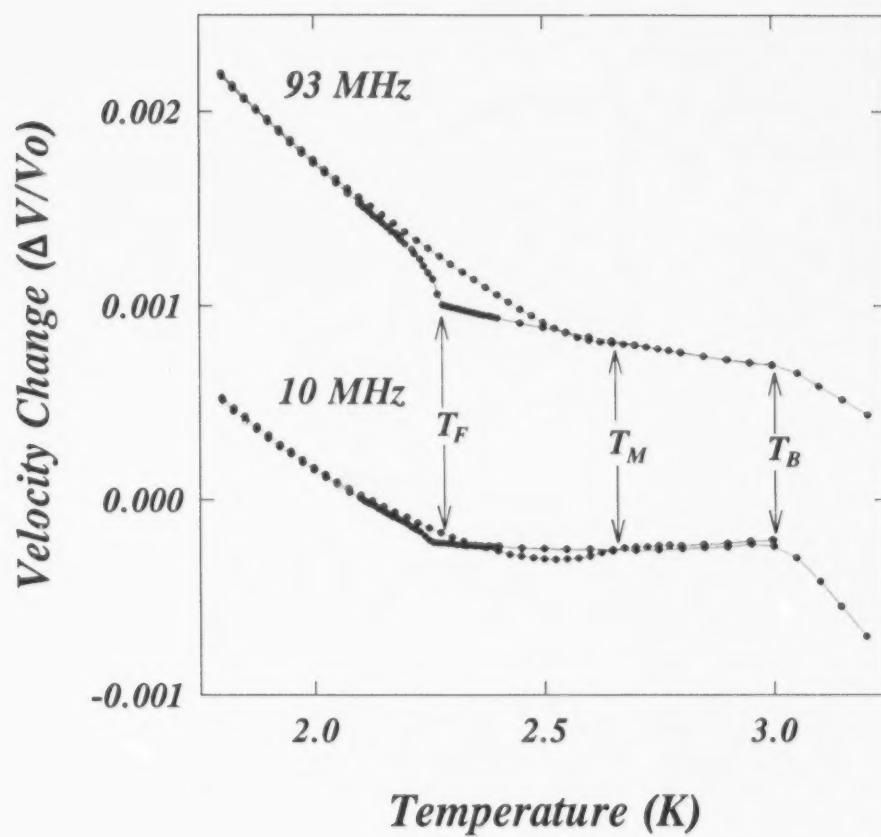


Figure 5.1.6 - Frequency-Dependence of the Hysteresis Region
 The hysteresis region is displayed for 93 MHz and 10 MHz showing the frequency-dependence of the shear modulus.

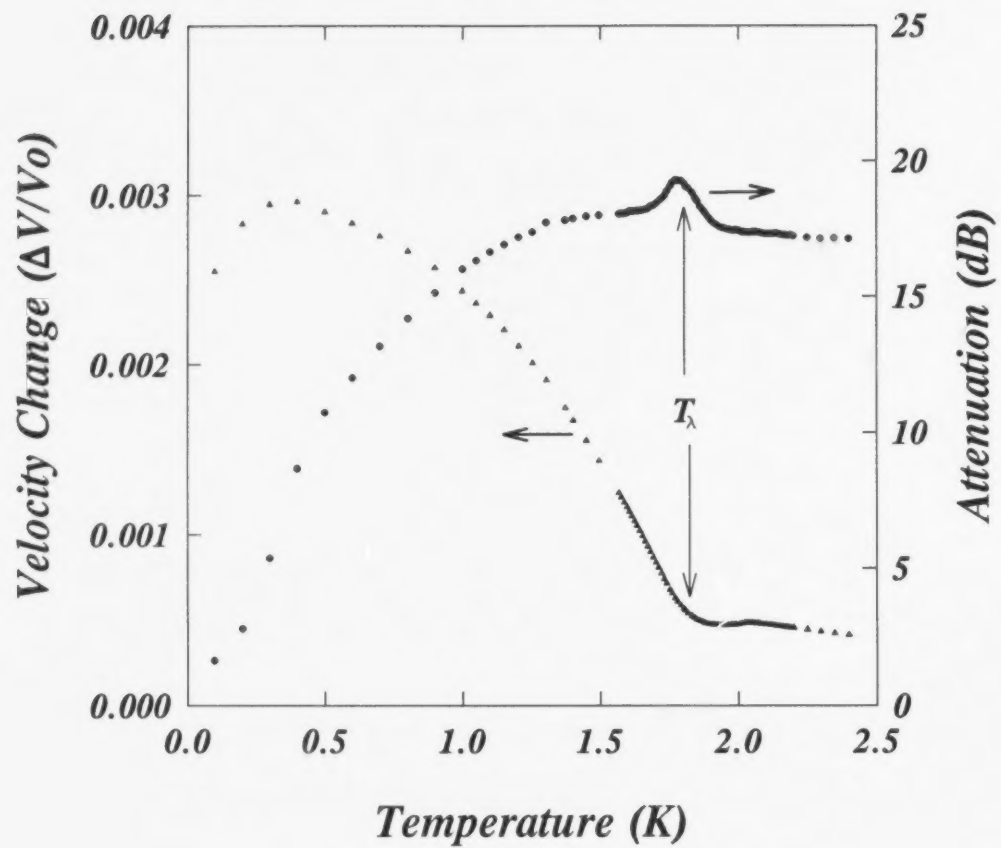


Figure 5.1.7 - Superfluid Transition in Vycor

The superfluid transition in Vycor is signaled by a rounded increase in 93 MHz sound velocity and a critical peak in attenuation.

the two previous scans (Figures 5.1.1 and 5.1.7) and above the bulk melting curve minimum. Figure 5.1.8 shows 93 MHz sound velocity and attenuation cooling curves at 36.65 bar and indicates just such a scenario. After bulk freezing at 1.972 K (T_B), the liquid helium in the pores undercools. Near 1.45 K, the superfluid transition (T_λ) in the pores occurs as the sound velocity increases and the attenuation peaks. In bulk systems, superfluid helium does not exist at these temperatures and pressures. Freezing in the pores begins at 1.30 K (T_F) as the sound velocity decreases and the attenuation increases. The sound velocity decrease is a density effect. By 1.30 K, a reasonable fraction of the confined liquid has become superfluid. Any solid must then form at the expense of already decoupled superfluid helium. The density contribution to the sound velocity change due to solidification is no longer simply the density difference between solid and liquid helium. Rather, it includes the amount of decoupled superfluid in the volume of solid formed. Further, the presence of solid pieces of helium in the pores may increase the effective tortuosity and reduce the decoupled fraction. Since the total shear modulus of the solid helium cannot be realized until lowest temperatures, the density contribution dominates. The sound velocity increases sharply near 1.25 K, and may indicate the point of complete freezing in the pores. The velocity continues to rise as the solid helium in the pores stiffens due to vacancy "freezeout", and the glass background takes over.

Warming data for Figure 5.1.8 are shown in Figure 5.1.9. Again, considerable hysteresis is present as the warming and cooling curves deviate around 1.0 K. Melting (T_M) in the pores is complete around 1.80 K, so that the hysteresis region is at least as large as the higher pressure runs. However, notice that, unlike the higher pressure runs,

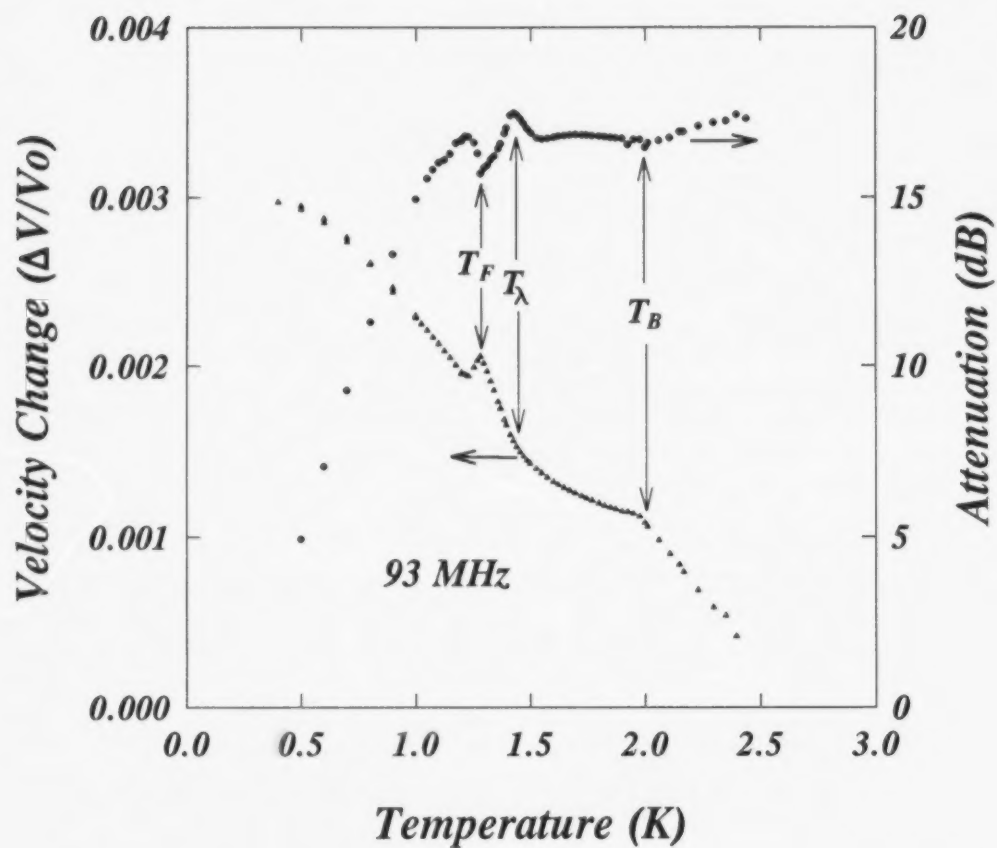


Figure 5.1.8 - Freezing and Superfluidity in Vycor
 Sound velocity and attenuation cooling curves at 93 MHz show superfluidity and freezing in Vycor.

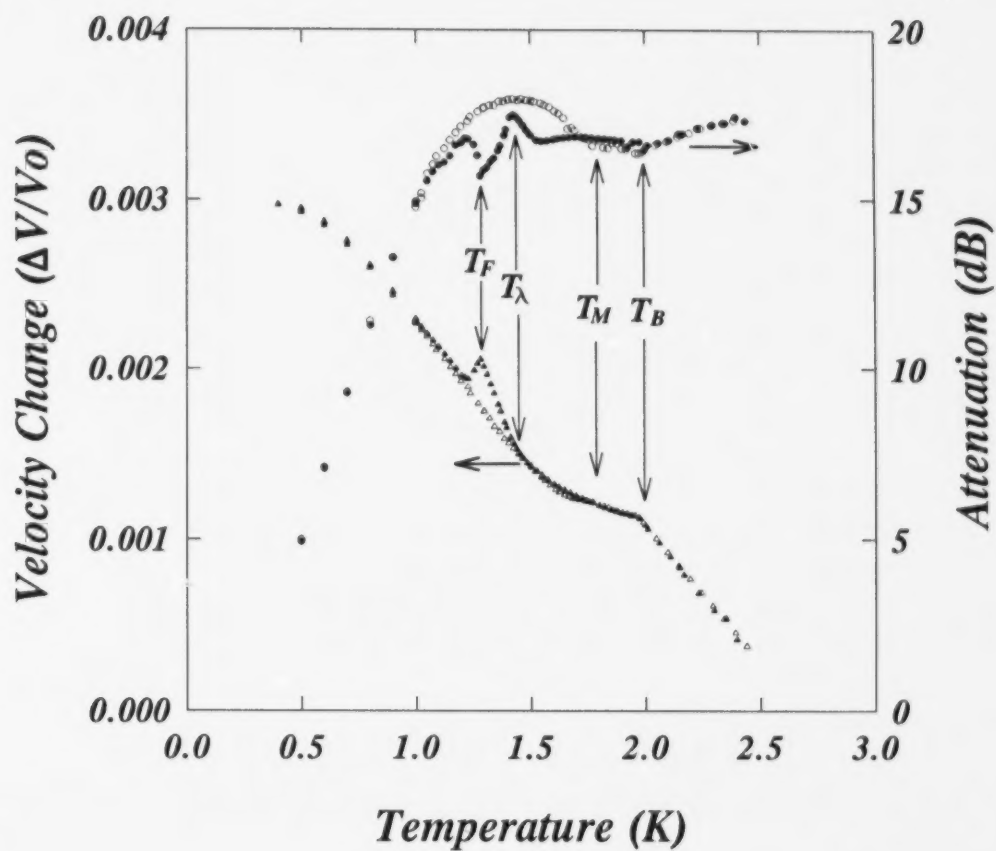


Figure 5.1.9 - Freezing, Melting, and Superfluidity in Vycor
 Sound velocity and attenuation warming and cooling curves at 93 MHz show hysteresis between freezing and melting with no superfluidity on warming.

the sound velocity is everywhere smaller on warming than cooling. This is not surprising given the huge recoupling effect of solidification. Also, on warming there is no evidence of a superfluid transition. This may suggest that even though freezing begins at 1.30 K, melting starts above 1.45 K, the superfluid transition.

Figure 5.1.10 is a family of 93 MHz superimposed sound velocity cooling curves done at slightly different pressures around the Vycor freezing curve minimum. Curve A is the lowest pressure, 35.78 bar, and has the superfluid transition at 1.45 K and no solidification. Curves B through F (solid circles) are done at successively higher starting pressures: 35.91, 35.95, 36.01, 36.41, and 36.65 bar, respectively. These curves trace curve A during superfluidity. Deviation from curve A (marked by arrows) indicates the start of freezing in the pores and occurs at increasingly higher temperatures for higher pressures. The sound velocity of any of these curves then stays below all lower pressure curves to lowest temperatures. Since the increased pressures can only increase the modulus contribution of the helium, this must be the density effect where solid helium recouples to motion of the Vycor. Therefore, to lowest temperatures, helium in the pores is a combination of liquid and solid with the solid component increasing with pressure. This behavior ceases at curve G (hollow dots connected by solid lines), at 37.68 bar, where freezing starts just below superfluidity. The sound velocity change is greater than the previous curve as zero temperature is approached. This may signal total freezing of helium in the pores as the modulus increase is larger than the density increase from curve F. A higher pressure scan (hollow circles connected by dashed lines), 43.6 bar, is included to demonstrate that the total velocity change continues to increase,

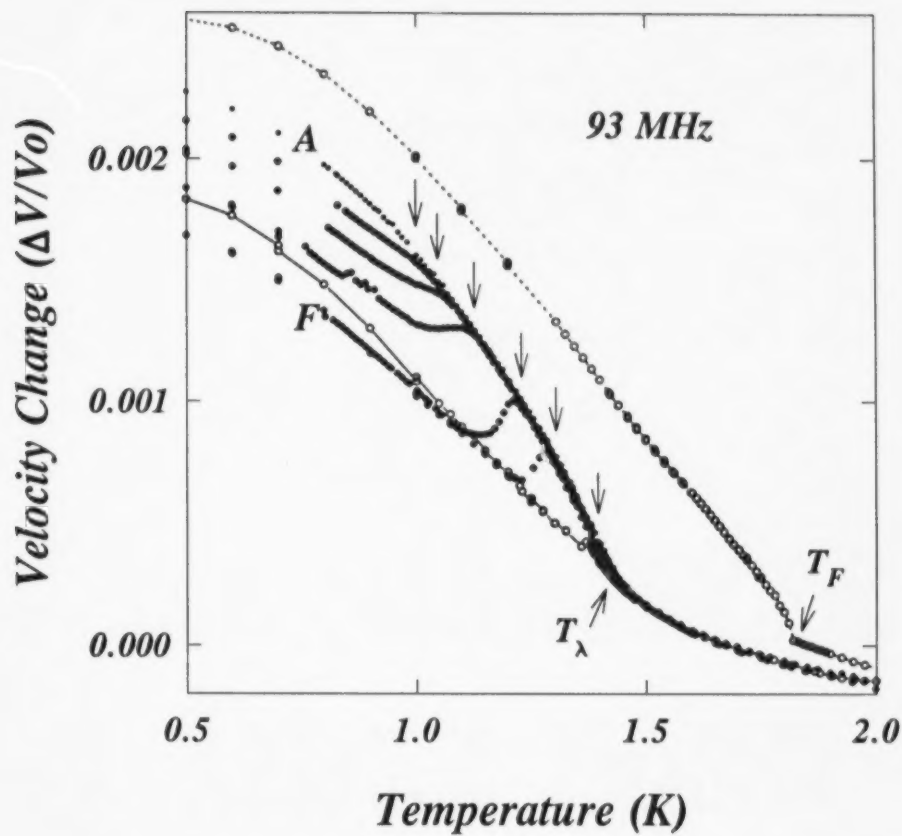


Figure 5.1.10 - Sound Velocity Near the Vycor Freezing Curve Minimum The family of 93 MHz sound velocity cooling curves shows nearly constant superfluid transition and pressure-dependence of freezing.

consistent with the increase in solid helium sound velocity with pressure.

Figure 5.1.10 contradicts two previous interpretations of experiments on helium in Vycor. Firstly, heat capacity measurements [8,12] suggested that not all helium in the pores freezes even at pressures significantly above the Vycor melting curve minimum. However, in this data, there appears a pressure, probably around curve G, where all helium in the pores has solidified. Further, in the higher pressure scans, there is no evidence of a superfluid transition. Secondly, torsional oscillator measurements of the superfluid transition at pressures above the bulk melting minimum showed a total period change that decreased with pressure implying that the superfluid density in Vycor decreases with pressure above the bulk melting curve and disappeared near 47 bar. However, the sound velocity curves A through F within the same pressure range trace each other until freezing starts. Thus, the superfluid density appears to be the same for each. Also, at 36 bar the amount that decoupled in the torsional oscillator experiment was half that at SVP. Here, at 36 bar, a total velocity change due to superfluidity is about 0.0020 and is 0.0003 greater than that at SVP [39]. This is expected given the density increase of the helium in the pores with pressure.

The behavior of the freezing curve minimum in Vycor can be gathered from Figure 5.1.10. Curve B is only about 0.1 bar higher than A. However, where freezing in pores in curve B occurs around 1.2 K, no freezing occurs in A. Thus, the freezing curve minimum in Vycor appears to be bulk-like in that for a pressure difference of only a small fraction of a bar solidification of helium can occur above 1 K or not at all.

The corresponding attenuation is displayed in Figure 5.1.11. The position of the

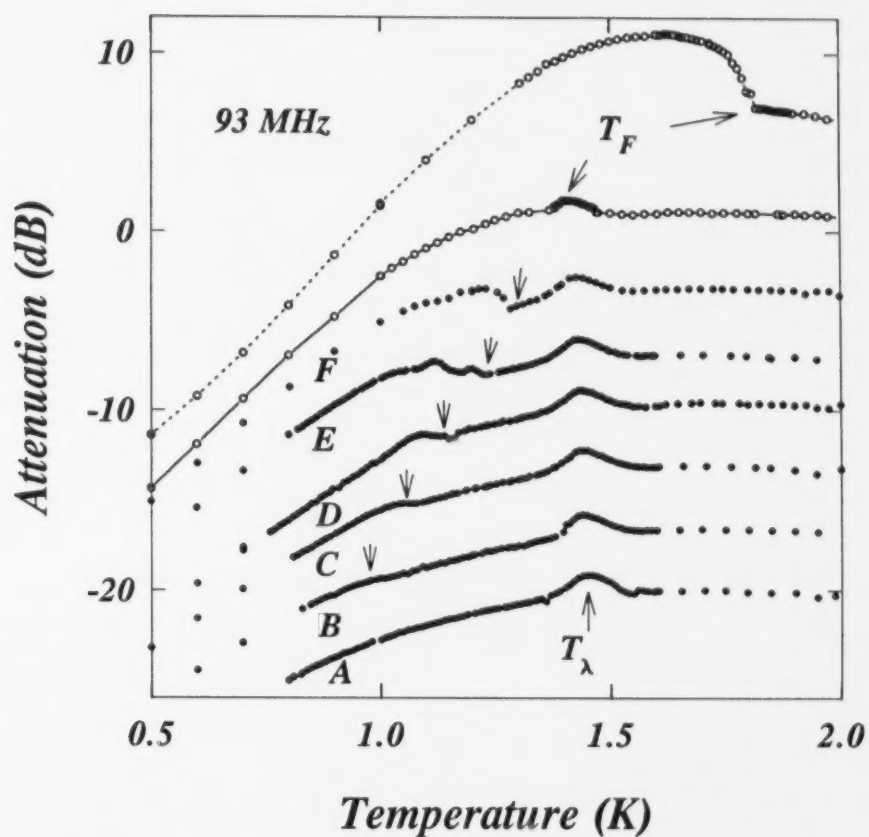


Figure 5.1.11 - Attenuation Near the Vycor Freezing Curve Minimum
 The family of 93 MHz attenuation cooling curves shows the nearly constant superfluid transition and the pressure-dependence of freezing.

critical peak changes very little in this pressure range. Meanwhile, freezing can occur as high as 1.45 K or not at all. Also, the height of the attenuation peak is about the same for each pressure, further suggesting that the superfluid density is the same for each.

The phase diagram for helium in Vycor is constructed from previous results in this dissertation and is a summary for helium in Vycor (Figure 5.1.12). The bulk melting curve and lambda line are solid. The dashed curves with solid and hollow circles are the Vycor freezing and melting curves, respectively. The Vycor lambda line is dotted. The freezing curve minimum in Vycor is about 11 bar above the bulk minimum. Meanwhile, the melting curve in Vycor appears to flatten at the same pressure but at higher temperature than the freezing curve. The Vycor lambda line crosses the Vycor melting curve slightly above the flat region and intersects the freezing curve substantially above the flat region. Therefore, there should exist pressures where superfluidity occurs on cooling but not on warming. This is demonstrated in Figure 5.1.9.

5.2 - Helium in Silica Aerogel

All helium in silica aerogel data were taken on one sample, 0.29 centimeter long, 85% porous, and with 20 MHz longitudinal transducers attached. Only a longitudinal pulse was produced with no shear component. Unlike Vycor, freezing helium in silica

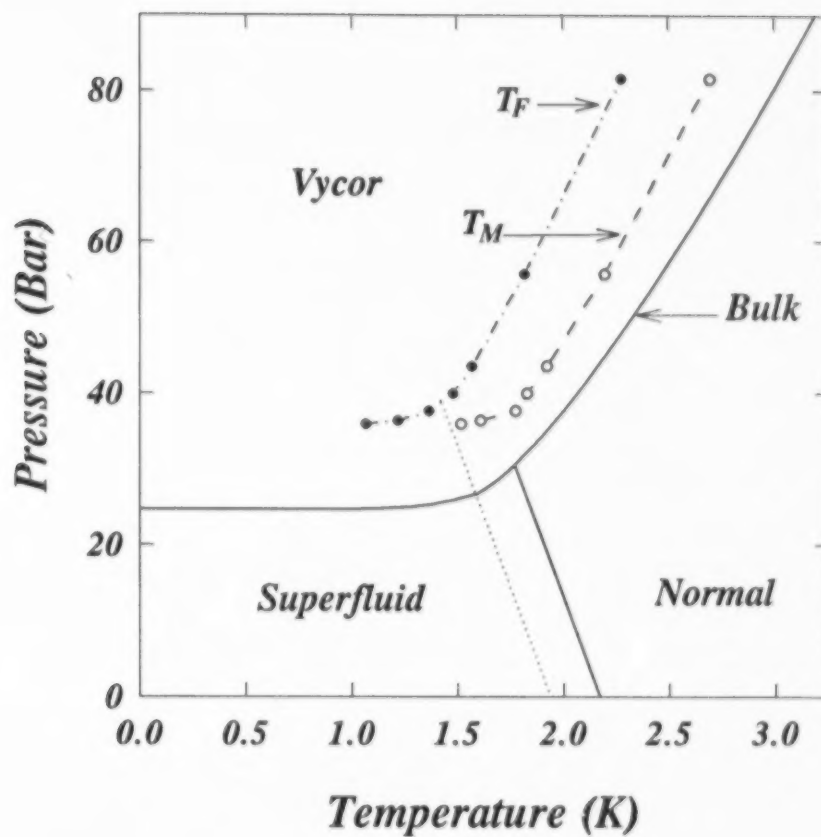


Figure 5.1.12 - Phase Diagram for Helium in Vycor
 The phase diagram for helium in Vycor shows the effect of confinement on the freezing and melting curves and the lambda line.

aerogel has never been studied. Some potential problems existed.

The first problem to be addressed in studying freezing and superfluidity of helium in silica aerogel was whether the delicate microstructure would withstand having liquid-solid helium interfaces in the pores. Recall that pressure gradients from most liquid-vapor interfaces crumble even high density aerogels. However, the aerogel sample survived freezing and melting in the pores during preliminary scans.

Another concern was the signal size. A typical low temperature signal in silica aerogel is considerably smaller than in Vycor. Only signals of 15 MHz and below were reasonably large at 4.2 K and odd harmonics of the fundamental were out of the question. Preliminary scans also indicated that solid helium in the pores has a large dissipation mechanism. Since this attenuation scales with frequency, only signals of 9 MHz and lower survived to lowest temperatures.

Having overcome these hazards, data were taken. The highest pressure scan produced the 9 MHz sound velocity (triangles) and attenuation (circles) cooling curves displayed in Figure 5.2.1. The scan begins at 2.35 K, in the middle of bulk freezing which, in contrast to Vycor, is seen as a rapid sound velocity decrease. This is due to using a longitudinal mode. Helium exiting the pores during bulk freezing reduces not only the total density but the compressional modulus as well. The loss of compressional modulus is greater and the sound velocity slows. At 2.27 K and 47.7 bar, kinks in velocity and attenuation indicate that bulk freezing (T_b) has completed. The liquid in the pores then undercools until 2.11 K, where freezing in the pores (T_f) is signaled by a sudden increase in sound velocity and attenuation. The undercooling of 0.16 K is

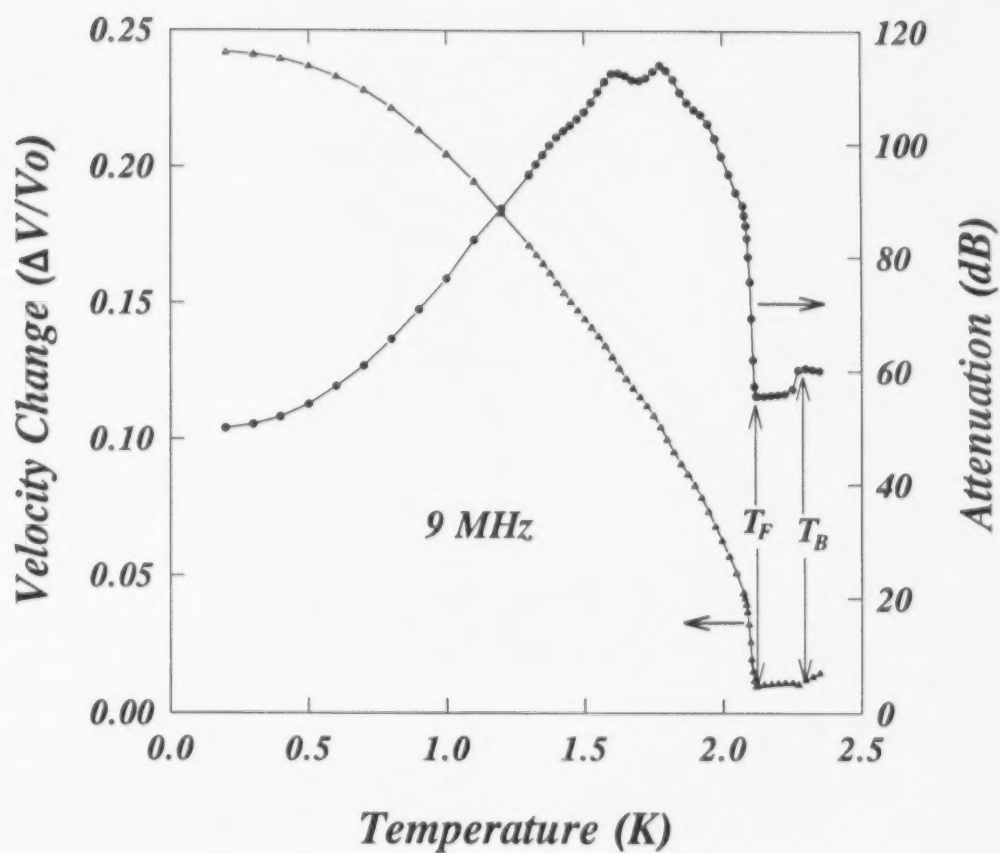


Figure 5.2.1 - Freezing of Helium in Aerogel

Sound velocity and attenuation at 9 MHz show helium in aerogel freezing below bulk.

considerably smaller than Vycor and, based on the homogeneous nucleation model, is consistent with pores about 5 times larger than Vycor. The sound velocity and attenuation increase much more rapidly during freezing in aerogel than in Vycor. This is not surprising since the largest pores, which freeze first, make up a significant volume fraction of the aerogel's pore volume.

Below T_F , the velocity and attenuation characteristics are similar to those of Vycor. There is no clear indication of the completion of freezing. Also, the sound velocity continues to increase to a total change of 0.23 at lowest temperatures and the attenuation peaks near 1.6 K. (The wiggles in the attenuation at the peak are experimental artifacts. Here the size of signal has become smaller than the linear range of the quadrature detector and each wave represents a 2π phase change.) Overall, sound velocity and attenuation changes in aerogel are much larger than in Vycor. This is expected since the highly porous aerogel has density and a compression modulus comparable to liquid and solid helium. A quantitative prediction of the velocity change due to freezing can be done. The modulus contribution from freezing is estimated by applying equation 2.9 to the liquid helium-filled and solid helium-filled cases. Notice that equation 2.9 was introduced to calculate the shear modulus increase from freezing in Vycor. The total modulus here involves both shear and bulk moduli. Equation 2.9 provides then only an approximation of the total modulus increase. For complete solidification of helium at about 50 bar in 85% porous aerogel, a velocity change of about 0.12 is expected, still considerably smaller than the measured change. However, equation 2.9 describes a situation of a material with basically uniform pores (i.e. like

Vycor) so that the amount of total strain from a passing stress wave that occurs in the pores is divided equally among the pores. Aerogel, due to its wide range of void sizes and irregular microstructure, should have regions that are elastic "weak links". That is, most of the total strain is found in only a fraction of voids. Thus, as freezing occurs in these regions, a larger velocity change than predicted by equation 2.9 is possible. Note that in the limit of $\phi \rightarrow 1$, the velocity change must be just that from liquid to solid helium, about 0.3.

This sound velocity and attenuation behavior may be due to mobile vacancies as in Vycor. The peak temperature increases with frequency and pressure as expected. Also, since aerogel voids are generally larger than pores in Vycor, typical vacancy pathlengths are longer in response to external stress. Thus, characteristic relaxation times for solid helium in aerogel should be longer than in Vycor. For a given pressure and frequency, the attenuation peak in aerogel should occur at higher temperature than Vycor. The results are consistent with this argument. Unfortunately, activation energies for vacancies cannot be deduced as in Vycor. The limited frequency range, the difficulty in picking precise peak temperatures, and some other peculiarities make a plot similar to Figure 5.1.4 impossible.

Warming data (hollow symbols) are superimposed in Figure 5.2.2. Hysteresis is still present but appears to be less pronounced than in Vycor. The size of the hysteresis region is unclear since the sound velocity on warming first deviates from cooling near 1.5 K while the attenuation warming data trace cooling until over 2.0 K. In either case, at 2.20 K, helium in the pores has completely melted (T_M).

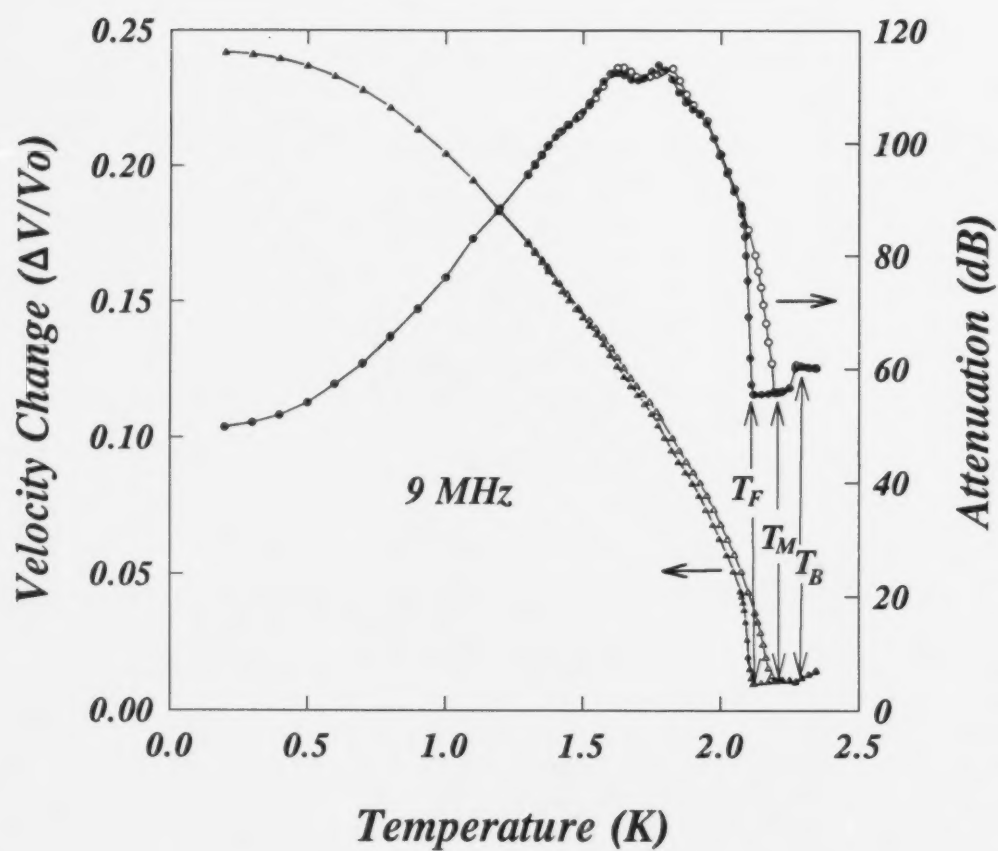


Figure 5.2.2 - Freezing and Melting of Helium in Aerogel
 Sound velocity and attenuation at 9 MHz show hysteresis between freezing and melting with the temperature of complete melting T_M below T_B .

Figure 5.2.3, an enlargement of the hysteresis region, shows similarities to Vycor. Despite a very open geometry with various void sizes and shapes, the onset of freezing T_F and completion of melting T_M in the pores appear very sharp in the sound velocity and attenuation. The completion of melting (T_M) is again about halfway between T_B and T_F .

The aerogel hysteresis region has some subtle differences from that of Vycor. Clearly there is a much more pronounced change in the slope of the cooling curves a few hundredths of a degree below T_F in aerogel. This temperature of slope change corresponds to the start of the hysteresis in attenuation and may be the completion of freezing in the aerogel. The sound velocity on warming deviates from cooling well below what appears to be the completion of freezing and the start of melting. The mechanism for this is unclear although similar behavior was observed for freezing argon in Vycor [2]. Notice that, unlike Vycor, the sound velocity during warming never dips below cooling. However, where the dip in sound velocity is seen in Vycor, the sound velocity curve in aerogel becomes slightly rounded just below T_M rather than approaching T_M with the same slope. This further suggests that vacancy motion does affect the compressional modulus of helium in aerogel like the shear modulus of helium in Vycor, although to a lesser degree. More evidence of significant stress relaxation via vacancy diffusion in aerogel is provided in Figure 5.2.4. Here 5 MHz (hollow circles connected by solid lines) and 9 MHz (solid circles connected by dots) sound velocities for the 47.7 bar scan show the frequency dependence of the transition. Everywhere there is solid helium in the voids, the 9 MHz velocity change is greater, indicating that solid helium

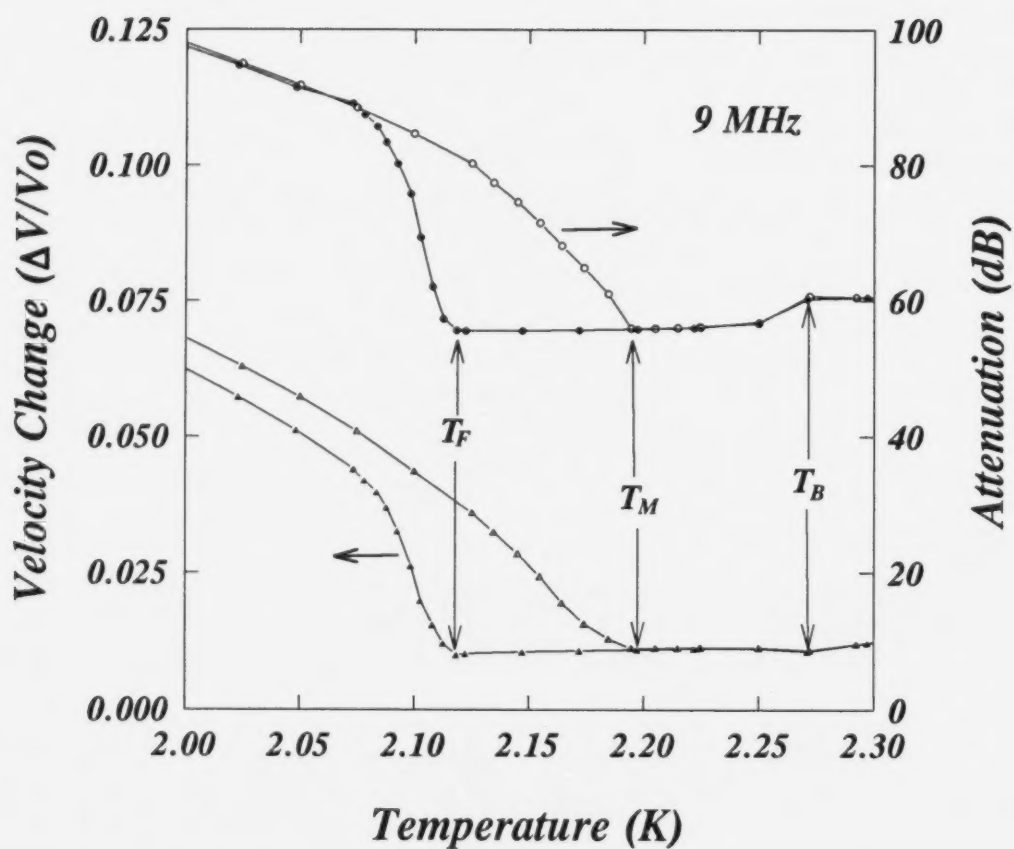


Figure 5.2.3 - Enlargement of the Hysteresis Region in Aerogel
 An enlargement of the hysteresis region shows sharp freezing and melting points with complete melting about halfway between freezing in aerogel and bulk.

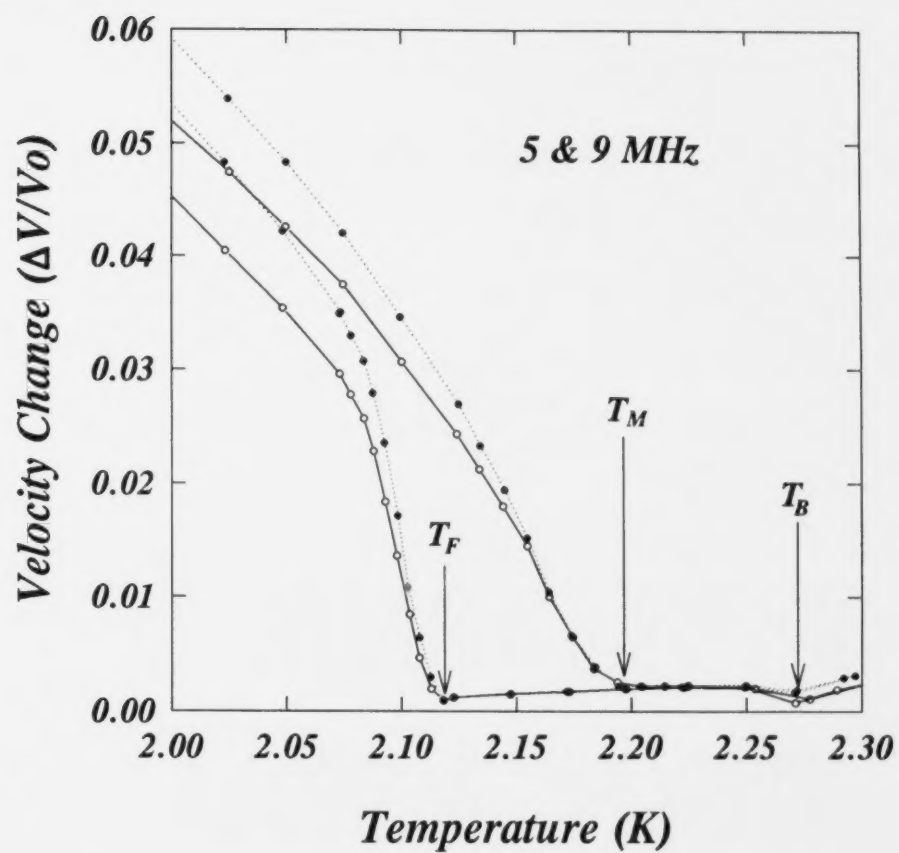


Figure 5.2.4 - Frequency-Dependence of the Hysteresis Region
 The hysteresis region is displayed for 9 MHz and 5 MHz showing the frequency-dependence of the compressional modulus.

confined in the aerogel responds stiffer for higher frequency sound waves. The difference in the velocity change between the 5 and 9 MHz signals at 2.0 K is about 0.007 on both warming and cooling. This increases to over 0.015 at 1.7 K. At low temperatures, where vacancies are highly immobile, the sound velocity changes for 5 and 9 MHz approach but do not reach the same value. At 0.2 K, a 0.007 difference in the velocity change remains.

Having completed high pressure scans, superfluidity in aerogel was explored. Figure 5.2.5 shows sound velocity and attenuation data at 9 MHz and 29.930 bar, just below the freezing curve minimum. While there is no evidence of freezing, superfluidity (T_λ) in the aerogel is seen as the sharp increase in sound velocity at 1.74 K and the critical peak in attenuation. The attenuation peak is about 2 dB but is certainly affected somewhat by the completion of bulk freezing which occurs at basically the same temperature. A total velocity change associated with superfluidity of nearly 0.06 is observed, about a quarter of the change associated with freezing.

At slightly elevated pressure, 30.04 bar, both superfluidity and freezing are observed in aerogel. Figure 5.2.6 displays 9 MHz sound velocity and attenuation cooling curves. During cooling from 1.9 K, the completion of bulk freezing and superfluidity in the voids occur almost simultaneously near 1.74 K. The sound velocity increases sharply and is accompanied by a critical peak in attenuation barely discernable on this scale. After undercooling 0.18 K to 1.56 K, freezing in the pores begins. Initially the sound velocity decreases as the solid recouples previously superfluid helium. Also, solid helium at this temperature may be significantly more compressible than bulk due to

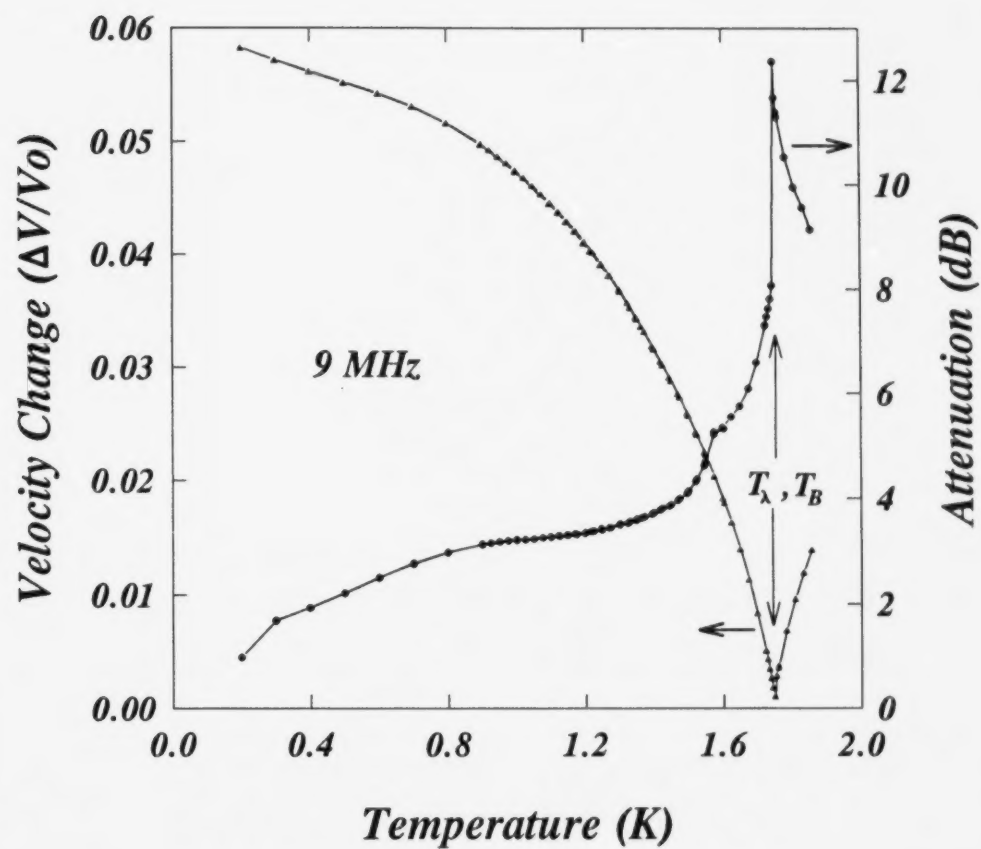


Figure 5.2.5 - Superfluid Transition in Aerogel

The superfluid transition in aerogel is signaled by sharp increase in 9 MHz sound velocity and a critical peak in attenuation.

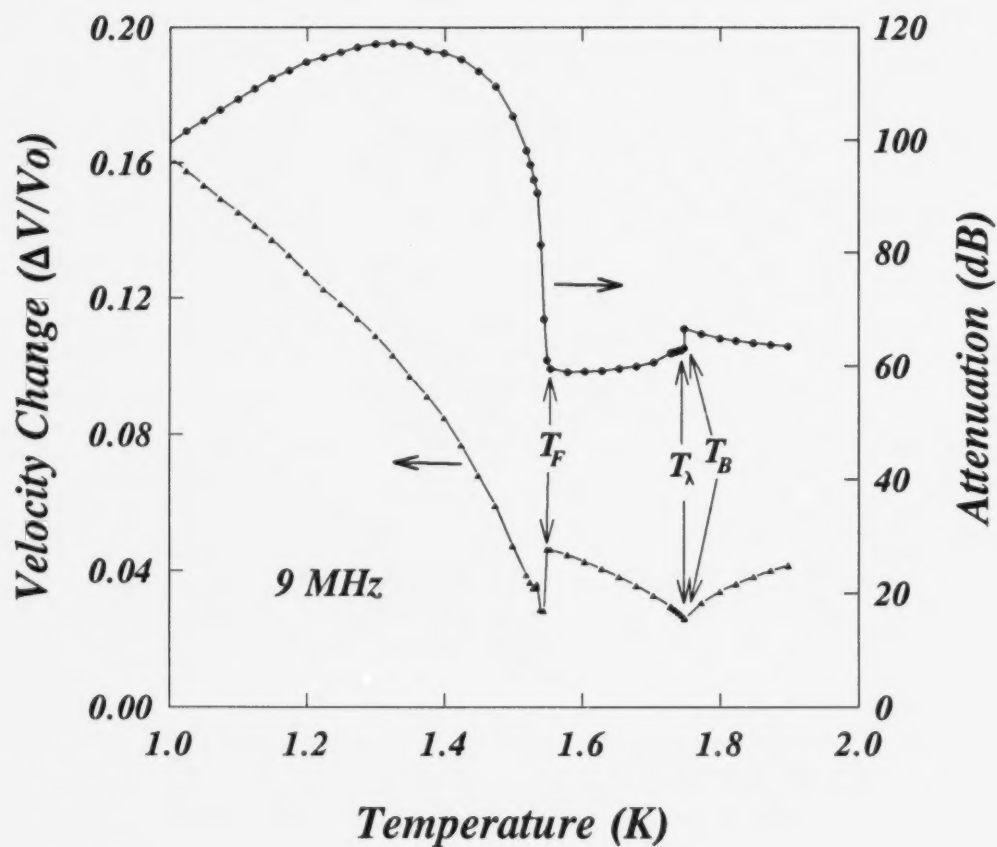


Figure 5.2.6 - Freezing and Superfluidity in Aerogel
 Sound velocity and attenuation cooling curves at 9 MHz show freezing and superfluidity in aerogel.

vacancy diffusion. Within a few hundredths of a degree of T_F , the sound velocity starts to increase and continues to lowest temperatures. By 0.2 K, the total velocity change is about 0.21, comparable with the 47.7 bar scan. This total velocity change is again much greater than that of the superfluid transition (0.06). Recall that near the freezing curve minimum in Vycor the superfluid transition had a greater velocity change. However, the modulus contribution of solid helium to the aerogel dominates the velocity change. Partial freezing in this system should be accompanied a significantly smaller velocity change. Presumably then, all the liquid in the aerogel solidifies at some temperature at this pressure with the slightly smaller decrease explained by pressure dependence of the helium compressional modulus.

Sound velocity and attenuation warming curves for Figure 5.2.6 are included in Figure 5.2.7. There is the expected hysteresis beginning as low as 1.0 K. The sound velocity on warming stays above cooling until 1.60 K. Then, as for Vycor, the warming sound velocity dips below cooling and eventually rejoins at 1.69 K, the completion of melting (T_M). Unlike Vycor however, this behavior only occurs when melting takes place below the superfluid transition. The attenuation on warming remains nearly constant until about 1.63 K. The attenuation then sharply peaks nearly 10 dB and rejoins cooling within a few hundredths of a degree. The temperature of the sharp attenuation peak corresponds to the sound velocity minimum on warming.

The warming data can be interpreted similar to those for cooling. All or most of melting takes place just below T_M . The majority of the sound velocity decrease is due to helium in the voids becoming more compressible with increased vacancy motion.

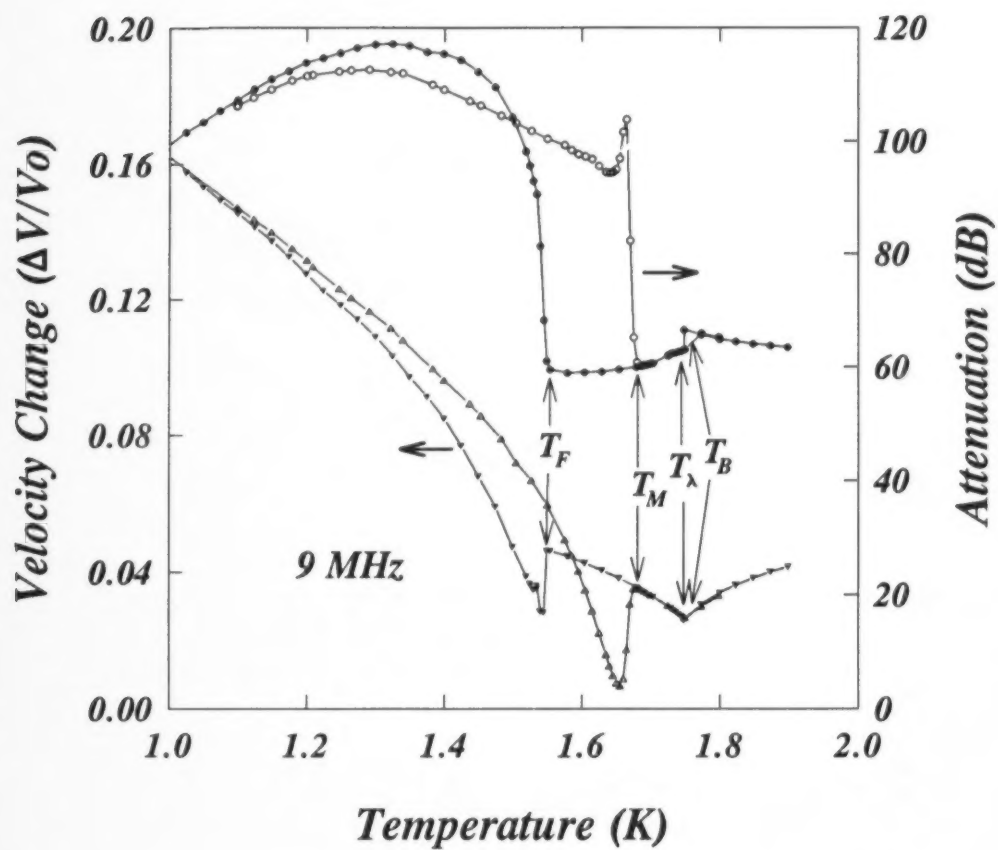


Figure 5.2.7 - Freezing, Melting, and Superfluidity of Helium in Aerogel Sound velocity and attenuation warming and cooling curves at 9 MHz show superfluidity and hysteresis between freezing and melting.

Eventually, in fact, the modulus increase from having solid present is less than the density decrease due to decoupled superfluid. When significant melting starts, the sound velocity stops slowing and eventually increases until T_M . The origin of the sharp attenuation peak is not clear. The peak is associated with superfluid in the pores but not the superfluid transition itself. That is, it is most significant when some combination of solid and superfluid helium are confined in aerogel. The peak is not thermally activated although it always appears just below T_M . One possibility involves the transmission of sound across the solid-superfluid helium interfaces that certainly exist in the aerogel. It has been shown [55-56] that a first sound wave is transformed into both first and second sounds at such an interface. This transformation would cause the large losses in signal amplitude observed during melting. A similar peak is observed just below T_F at lower pressure.

Ignorance about the mechanism for this peak just below T_M does not prevent displaying several 9 MHz attenuation curves to see how the peak changes with melting temperature. Figure 2.5.8 shows curves A through F done at 33.76, 32.72, 31.28, 30.76, 30.04, and 29.95 bar respectively. In curve A, where T_M is about 1.82 K, well above T_λ , the attenuation is monotonically decreasing just below T_M . Still, there is a drastic 10 dB drop only a few hundredths of a degree below T_M . Curve B, with T_M around 1.79 K, has a visible peak and a somewhat larger attenuation drop than curve A. Curve C has a melting temperature very near that of the superfluid transition, 1.74 K. Here, the attenuation peak is the largest of all curves and the attenuation drops over 50 dB between the peak and T_M . In curves D through F, the peak always occurs only a few

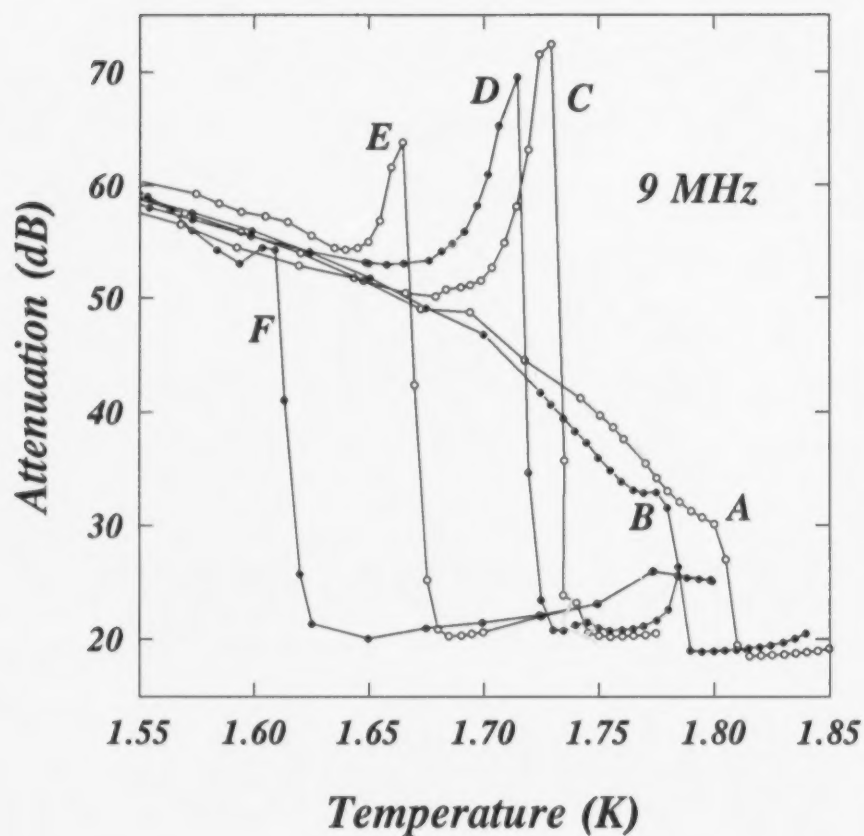


Figure 5.2.8 - Attenuation Peaks During Melting

Attenuation in 9 MHz sound has peaks immediately below the melting temperature that increase in size as the superfluid transition temperature is approached.

hundredths of a degrees below T_M but the height of the peak gets progressively smaller with melting temperature. This is interesting since as T_M is reduced, any liquid in the aerogel has a larger superfluid component. Curve F, in fact, has almost no peak at all.

A family of sound velocity cooling curves near the aerogel freezing curve minimum is shown in Figure 5.2.9. The pressures for curves A to F are 32.74, 30.76, 30.04, 29.950, 29.945, and 29.930 bar. Like Vycor, the lambda point of aerogel, 1.74 K, changes very little in this pressure range. The curves overlap below T_λ until T_F , the start of solidification in the voids. The freezing point shifts to significantly lower temperatures until curve F, where no solidification in the voids occurs. Notice that, unlike Vycor, the total sound velocity change is always greater for higher pressure scans. Also, curve E, where freezing in the pores begins around 1.25 K, was done only a small fraction of bar higher in pressure than curve F, where no freezing the pores occurs.

A variety of different behaviors are seen below T_F . For curve A, like higher pressure scans, the freezing process is seen as a monotonically increasing sound velocity. This is not surprising since the superfluid fraction in the aerogel is small at T_F so that little recoupling happens. The next two curves, B and C, have higher superfluid densities at T_F . Here solidification initially lowers the sound velocity before the modulus contribution, perhaps in the form of reduced vacancy motion, takes over. Freezing in Curve D has unexpected characteristics. The sound velocity initially increases due to solidification although the superfluid density in the aerogel is greater than preceding curves. The sound velocity then decreases, dips slightly below curve F, and then starts the continuous increase to lowest temperatures. Curve E has no region of velocity

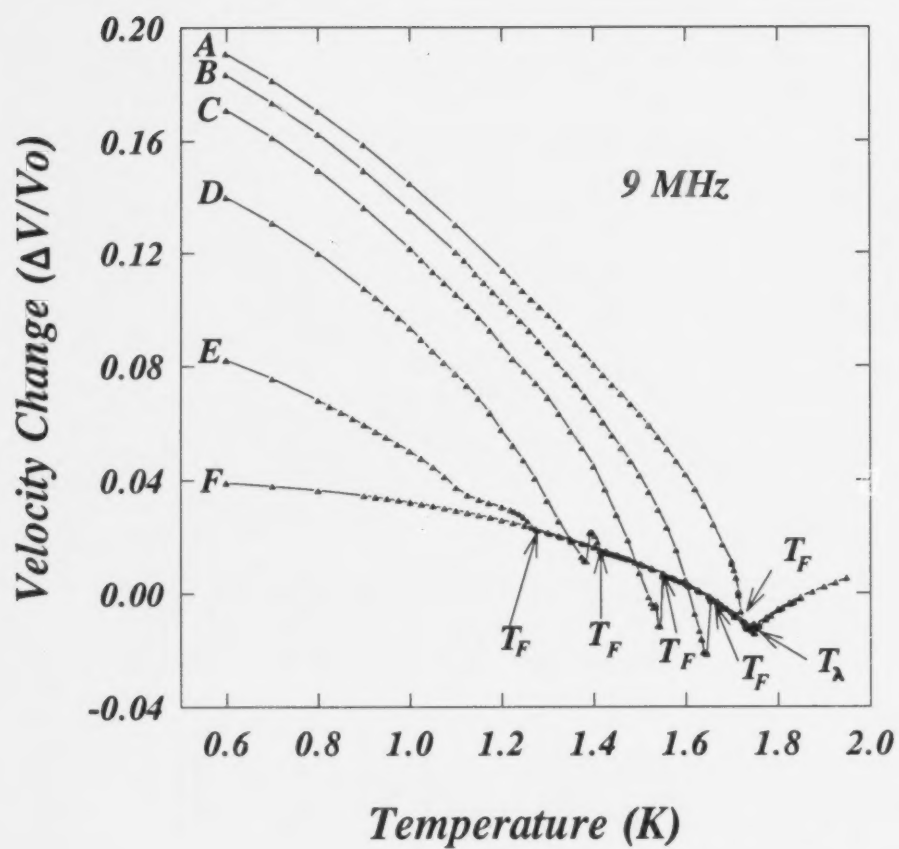


Figure 5.2.9 - Sound Velocity near the Freezing Curve Minimum in Aerogel The family of 9 MHz sound velocity cooling curves show a nearly constant superfluid transition and pressure-dependence of freezing.

decrease. One possible explanation is that any solid helium that forms in the aerogel is much stiffer at these low temperatures such that the competing density effect of recoupling is overcome.

The total velocity change at the lowest temperatures from the previous scans gives information about the frozen fraction of helium in the voids. Figure 5.2.10 compares Figure 5.2.9 (A through F) with Figure 5.2.6 (G) done at higher pressure. For curves A and B, the total velocity change is comparable to higher pressure scans with differences explained by the pressure dependence of the helium compressional modulus. Most, if not all, of the helium in the aerogel has presumably solidified at these pressures. However, Curves D and E are only fractions of the higher pressure scans. Clearly, some of the solid helium compressional modulus is missing as liquid remains in the pores. In summary, for aerogel, like Vycor, there appears to be a narrow pressure range, about 29.930 to 30.76 bar, where freezing occurs but not all of the confined helium solidifies.

Corresponding attenuation data are presented in Figure 5.2.11 and only a few features are worth noting. For Curves A through D, most of the total attenuation happens within a few hundredths of a degree below T_F . The attenuation increase in Curve E is more gradual. The attenuation for Curves A and B almost overlap below 1.6 K. Meanwhile, the behavior of all subsequent lower pressure scans is unique from all others. This further suggests that freezing has completed for Curves A and B but remains incomplete for all lower pressure scans. Interestingly, only Curve D has an attenuation peak like that observed on melting.

Based on these results, a phase diagram for helium in aerogel can be constructed

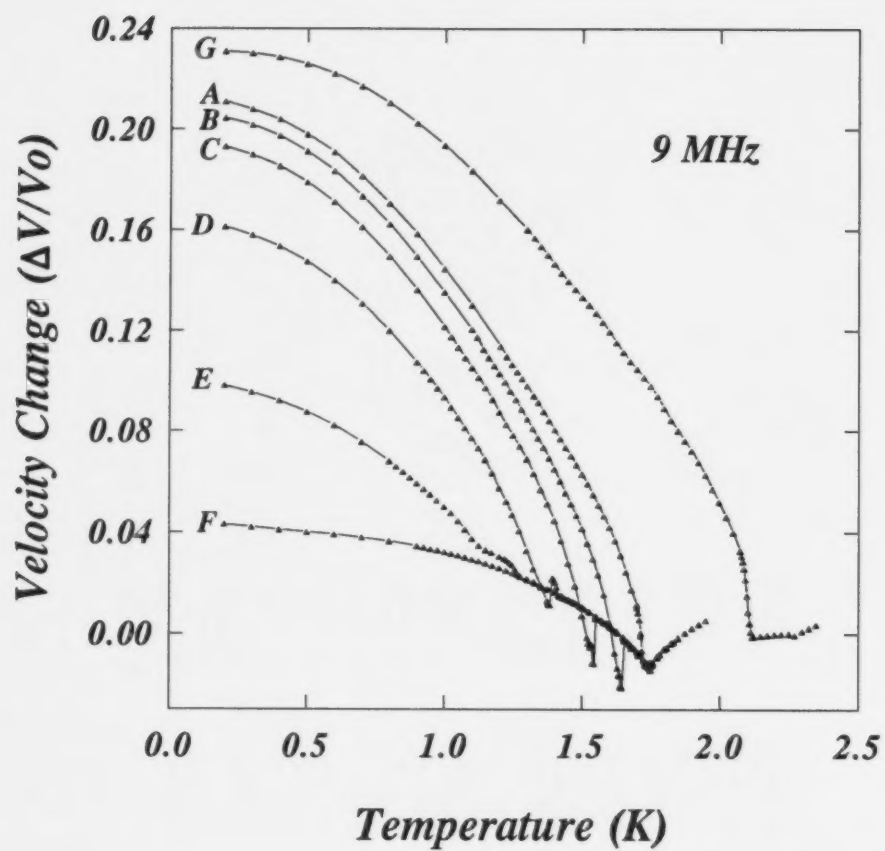


Figure 5.2.10 - Sound Velocity During Freezing at Various Pressure
 The total sound velocity change stays nearly the same until near the Aerogel freezing curve minimum.

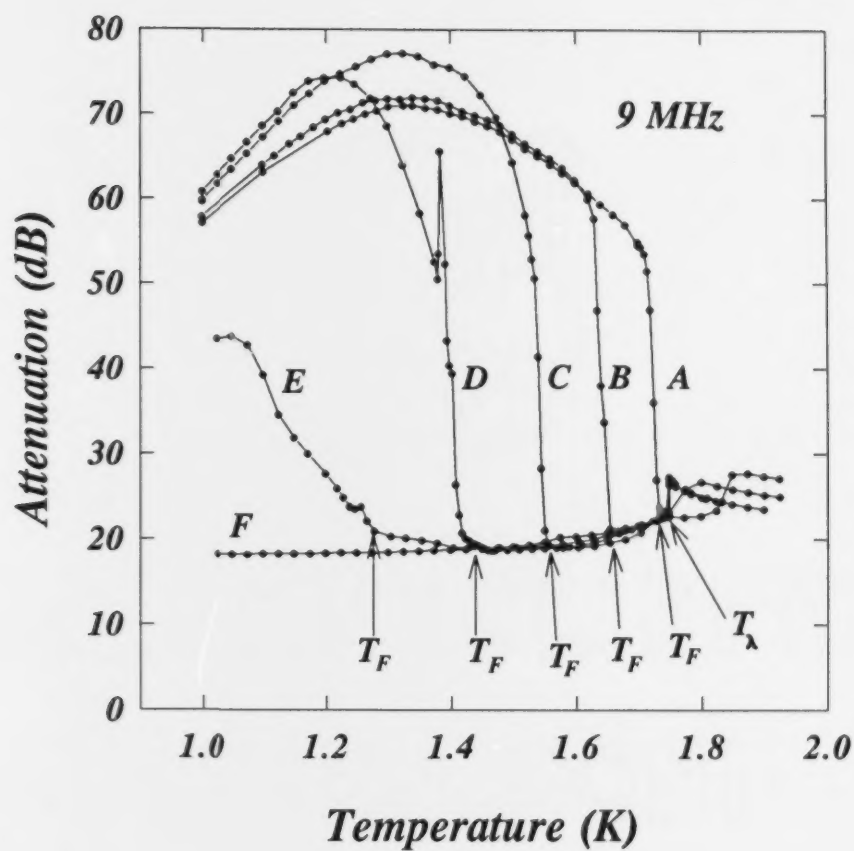


Figure 5.2.11 - Attenuation near the Aerogel Freezing Curve Minimum The family of 9 MHz attenuation cooling curves shows the nearly constant superfluid transition and the pressure-dependence of freezing.

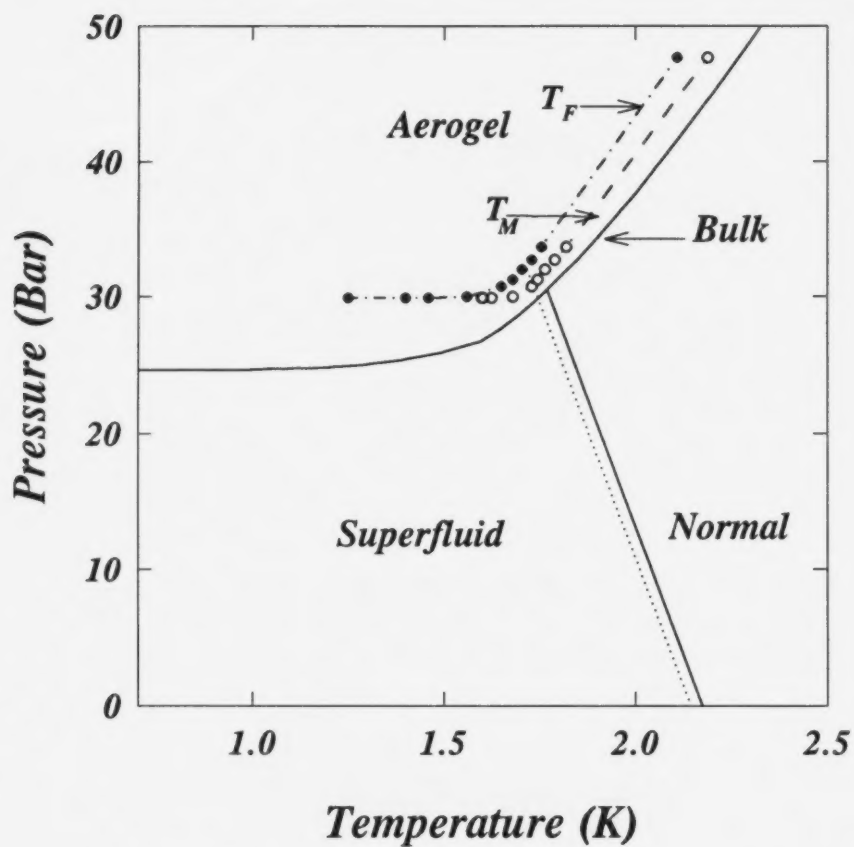


Figure 5.2.12 - Phase Diagram of Helium in Aerogel
 The phase diagram of helium in aerogel shows the effect of confinement on the freezing and melting curves and the lambda line.

(Figure 5.2.12). The bulk melting curve and lambda line are solid. The aerogel freezing and melting curves are dashed with dots and dashed, respectively. The aerogel lambda line is dotted. Clearly, aerogel with larger voids and a more open geometry, is closer to a bulk system than Vycor. Whereas the freezing and melting curve minima are about 35.9 bar in Vycor, helium will solidify in this particular aerogel as low as 29.9 bar. The melting curve is about halfway between the freezing curve and bulk. The melting curve flattens at the same pressure as but at higher temperature than the freezing curve. The aerogel lambda line is reduced to slightly lower temperatures but is parallel to bulk.

5.3 - Helium in Anopore Membranes

All data were taken on one sample, 1.9 centimeter long and 0.5 centimeter wide. Although shear transducers were used, both the L(1) longitudinal and SH(0) shear mode were visible. In addition, large distorted signals appear after the shear mode that may be several reflected modes superimposed. The first shear mode, in fact, may have some interference from reflections. The first longitudinal pulse was generally larger with minimal distortion and was used for the majority of data. Only a small frequency range, 5 to 15 MHz, was suitable for experimentation.

Like silica aerogel, freezing in Anopore Membranes has not previously been studied. Some obvious problems with using helium as the adsorbate existed. The cross-section of an Anopore sample has hardly any surface area to contact the transducers.

Sound can propagate not only in the Anopore Membrane but in the surrounding bulk solid or liquid helium as well. The received signal could have a component associated with the bulk. Fortunately, the sound speed in helium is at least six times slower than in Anopore and the sample is long enough that no interference from these modes should be possible. Also, loading of the sample and transducers by surrounding liquid or solid may drastically affect the signal. To alleviate this potential problem, argon was used in place of helium so that solidification could occur with essentially no surrounding bulk.

Early experiments were performed with argon since comparative ultrasonic studies in Vycor have been done in this lab [2]. The entire freezing and melting processes of argon in Anopore seemed to happen very suddenly, within a few tenths of a degree. Some hysteresis may have been present as melting temperatures seemed higher. Unfortunately, these transitions were within a few tenths of a degree of bulk so it was uncertain if bulk freezing (outside the pores) could be responsible for some of the effects. Also, with freezing in pores occurring so rapidly, the measured phase may change by several factors of π in a single data point. Although these can be added later, the correct number of π to add, and thus the total phase and velocity change, were never certain. Eventually, argon in Anopore experiments were abandoned and helium was used.

Early results showed that Anopore may produce results far different from Vycor and silica aerogel. For instance, while filling the sample with helium, the signal size drops about 20 dB for some frequencies. This may be an indication of being in the "high frequency regime" as discussed in Chapter 2, with the dissipation of sound due to Biot's sloshing mechanism. This was unexpected, particularly in the SH(0) mode, since

decoupling should be almost eliminated by the high tortuosity for this mode.

Once filled and pressurized, the 1 K pot was filled, blocking the fill capillary, and several scans were performed. Figure 5.3.1 shows typical 13 MHz longitudinal sound velocity and attenuation cooling curves. On cooling, the sound velocity starts to increase at 3.215 K. This is the start of bulk freezing in the cell (T_{SB}) as liquid begins to exit from the pores. No signature is present in attenuation as the signal size remains constant. Just below 2.50 K, near the expected completion of bulk freezing, the sound velocity and attenuation sharply increase. On continued cooling, the velocity peaks, drops to a minimum, and then mildly increases for about 0.1 K. Meanwhile, the attenuation appears basically like a step function with the plateau about 25 dB higher than original level. Since all these effects occur near the expected end of bulk freezing, it is unclear in Figure 5.3.1 which kink is the completion of bulk freezing and which, if any, is associated with freezing in the pores.

Fortunately, the temperature of the completion of bulk freezing (T_{EB}) can be measured. Since these experiments are performed at essentially constant bulk helium density in the cell, T_{EB} is unique for a given T_{SB} and independent of the volume of the cell. Thus, the temperature of the completion of bulk freezing for Anopore in the cell is the same as with any other porous material in the cell provided that T_{SB} is the same. Recall that for sound velocity of helium in Vycor, both the start and completion of bulk freezing are sharp, distinguishable features and can be determined to within a few mK. Therefore, Vycor will be used for comparison. There is a consideration involved with this measurement. With liquid exiting from the pores during bulk freezing, Vycor and

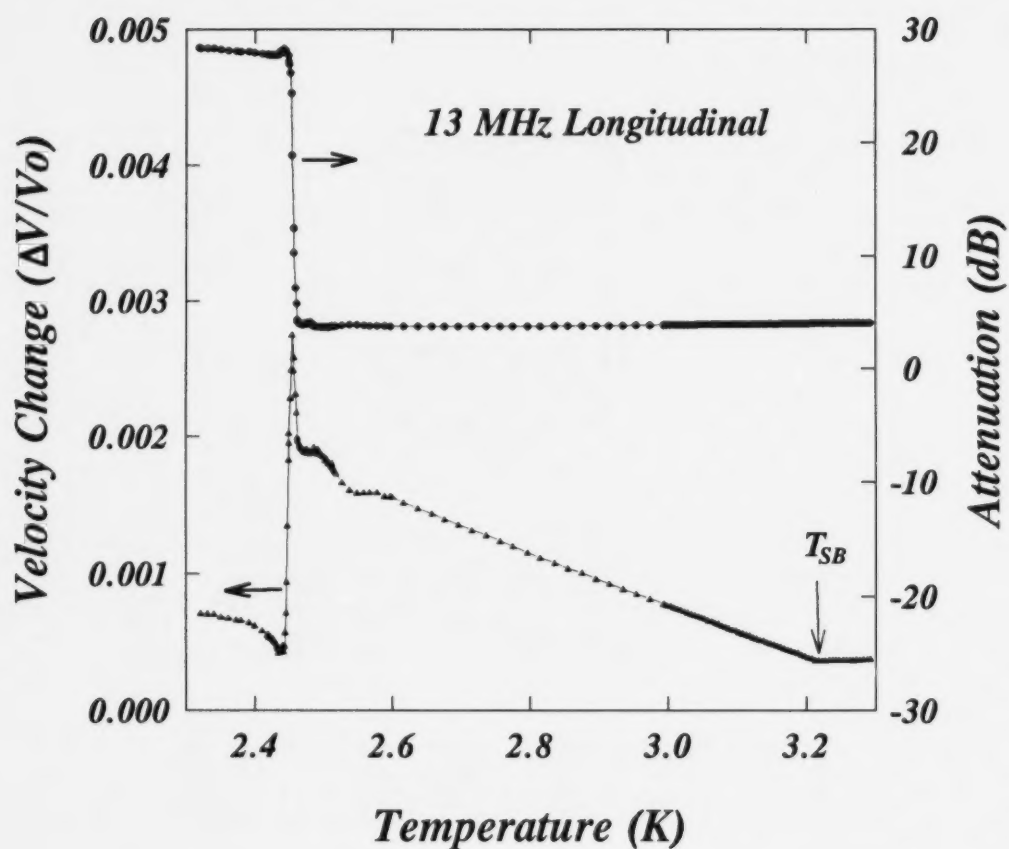


Figure 5.3.1 - Freezing Helium in Anopore.

Sound velocity and attenuation for 13 MHz longitudinal mode shows the start of bulk freezing (T_{SB}) and kinks near the completion of bulk freezing.

Anopore act as helium sources and the bulk density, along with T_{EB} , will increase slightly. Given that the cell is about 10 cc and the pore volume of a typical Vycor sample is about 0.1 cc, the change in bulk density during solidification is about 1.5×10^{-5} g/cc. This density increase would increase T_{EB} by less than 1 mK, which is within the uncertainty of the measurement of T_{EB} . Anopore, of course, is only 60 microns thick and so has negligible pore volume.

Figure 5.3.2 is an enlargement of Figure 5.3.1 and includes the sound velocity for helium in Vycor with the same T_{SB} to within 1 mK. The sudden sound velocity and attenuation increase (point A) coincide at 2.463 K. The sharp peak in sound velocity (point B) occurs at 2.455 K. There is no clear attenuation feature associated with point B. Below point B, the sound velocity sharply decreases until point C. Below point C, the sound velocity and attenuation become flat. Notice that the attenuation flattens slightly above the sound velocity.

Clearly, the sound velocity in the Vycor sample indicates that the completion of bulk freezing occurs at about 2.455 K, almost exactly where the sharp peak in the sound velocity occurs. Point B is thus identified as T_{EB} . Comparisons at other pressures were consistent with this result. This leaves the question of where freezing in the pores occurs.

Consider the sound velocity change for the longitudinal mode during bulk freezing. An upper limit of this velocity increase can be estimated by assuming that the density change of the liquid in the pores is the same as that of bulk and ignoring any compressional modulus change of the liquid in the pores. The expected velocity increase

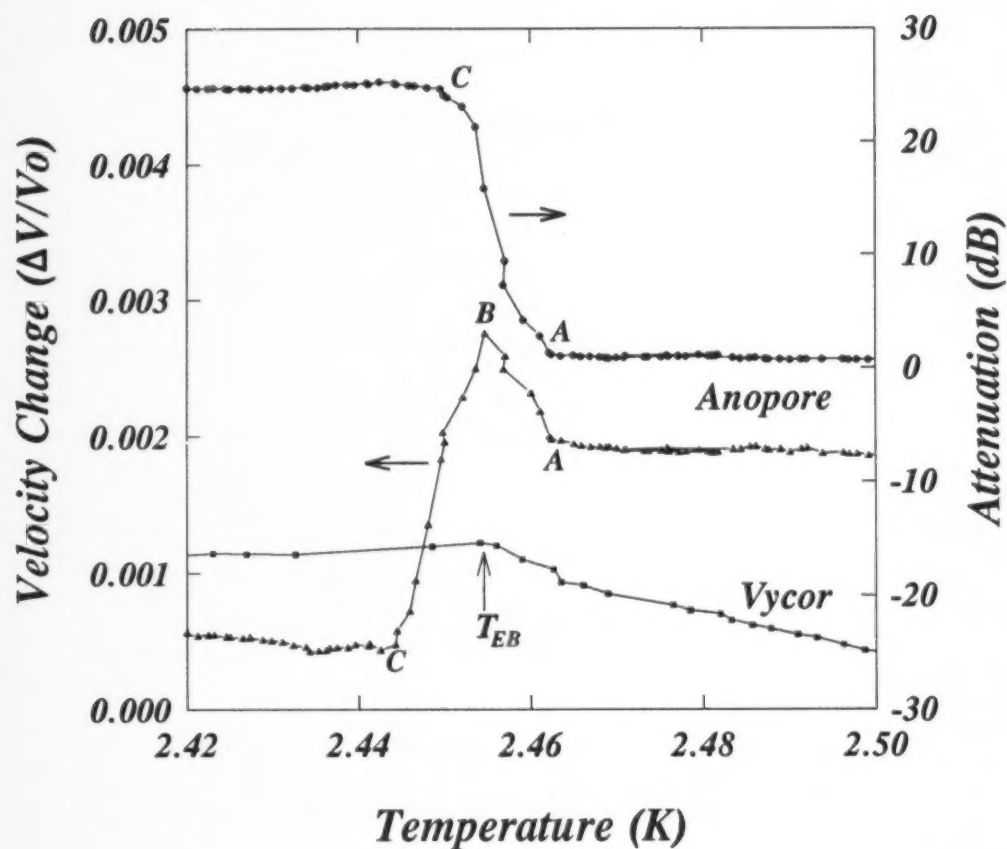


Figure 5.3.2 - Comparison of Anopore and Vycor Near the End of Bulk Freezing. The sound velocity for helium-filled Vycor shows that the peak in sound velocity in helium-filled Anopore (point B) corresponds to the completion of bulk freezing.

is, at most, 0.0015. In Figure 5.3.1, the measured velocity increase between T_{SB} and point A (T_{EB}) is nearly as calculated. However, between point A and T_{EB} , the sound velocity increases more rapidly so that the total velocity increase between the start and end of bulk freezing is about 0.0025. This suggests that the extra velocity increase may be caused by an interaction of the Anopore Membrane with the surrounding liquid or solid helium. As the L(1) mode propagates, the surface of the Anopore periodically flexes. Bulk helium, perhaps as far as a wavelength away, may be coupled to this motion. Changes in the surrounding bulk should affect the sound velocity. Still, the mechanism for the sharp kink at point A is unclear. A possible explanation is that the bulk solid does not perfectly wet the Anopore. At point A, just above the completion of bulk freezing, the solid helium begins to contact the Anopore. More evidence that point A is associated with bulk is shown in Figure 5.3.3. Recall that the attenuation increases sharply at point A rather than at T_{EB} . Notice that the attenuation for 5.5 MHz, 9 MHz, and 13 MHz longitudinal waves appears to be independent of frequency. This behavior, which is never observed during freezing in Vycor or aerogel, may be caused by the nature of a plate mode surrounded by bulk helium. As the plate mode propagates, the surrounding bulk must be coupled to some degree to the motion of the Anopore surface. The creation of this coupled motion in the bulk helium is a loss mechanism for the passing wave. That is, the Anopore essentially radiates some of the energy of the sound wave to the bulk helium, independent of frequency. How much energy is radiated depends on the relative acoustic impedances of the Anopore and the bulk helium. Clearly, the impedance match between solid helium and Anopore is closer than that of

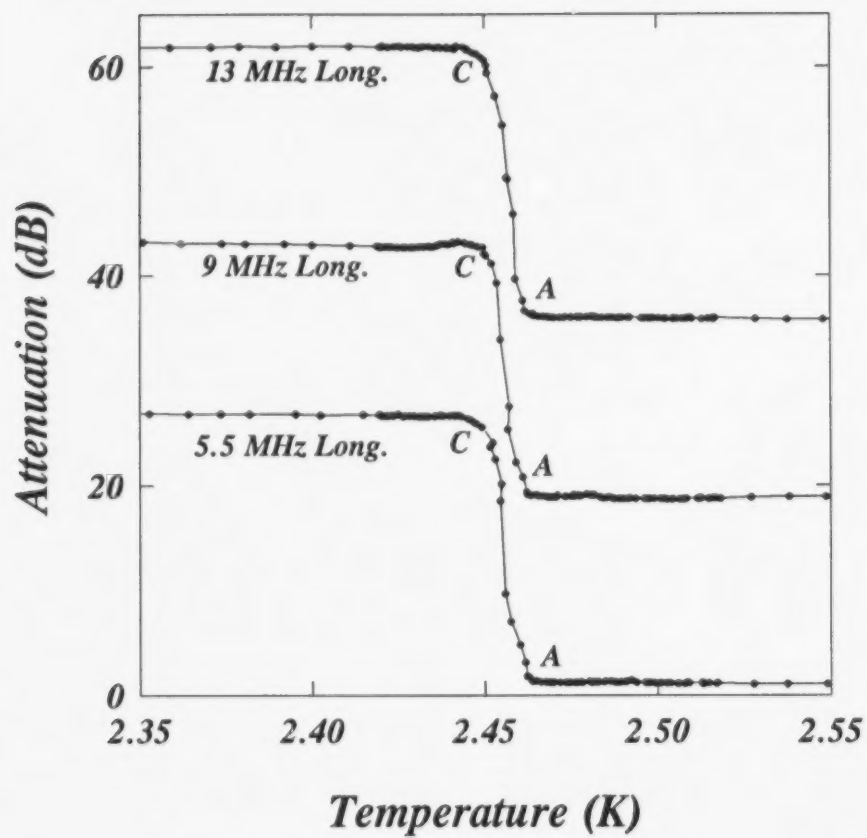


Figure 5.3.3 - Attenuation of Anopore Near the Completion of Bulk Freezing. The sound attenuation at 5.5, 9, and 13 MHz for the L(1) mode increases at point A and does not scale with frequency.

liquid helium and Anopore. Thus the amount of energy radiated increases and the attenuation in the sound wave increases, again independent of frequency. This also explains why the attenuation increases by about 20 dB when the cell was filled with liquid helium. No energy from the Anopore can be radiated to a surrounding vacuum.

To identify freezing in the pores, similar data were taken on 90 micron-thick (nonporous) aluminum foil with 20 MHz shear transducers. Aluminum was chosen because its longitudinal acoustic impedance ($1.3 \times 10^7 \text{ kg}/(\text{m}^2\text{s})$) is nearly that of the Anopore ($7.4 \times 10^6 \text{ kg}/(\text{m}^2\text{s})$) and thus basically the same acoustic match between bulk and sample is achieved. Again a longitudinal mode was excited. The sound velocity data from Figure 5.3.1 and for the aluminum foil at nearly the same filling pressure are displayed together in Figure 5.3.4. During cooling, the sound velocity in the aluminum foil actually decreases slightly during most of bulk freezing. This indicates that the velocity increase in the Anopore over the same range is due to helium in the pores. Near the end of bulk freezing, the aluminum foil has the same sharp velocity increase as the Anopore sample (point A). The sound velocity in the foil also has a similar peak at the completion of bulk freezing. However, below T_{EB} the curves appear quite different. The aluminum foil's sound speed drops much more gradually and has no sharp kink below T_{EB} (point C).

The attenuation of the longitudinal mode in the Anopore Membrane and in the aluminum foil are compared in Figure 5.4.5. As with the Anopore, the attenuation in the aluminum foil (squares) increases suddenly near the completion of bulk freezing and by a similar amount. This demonstrates that the same mechanism for the attenuation

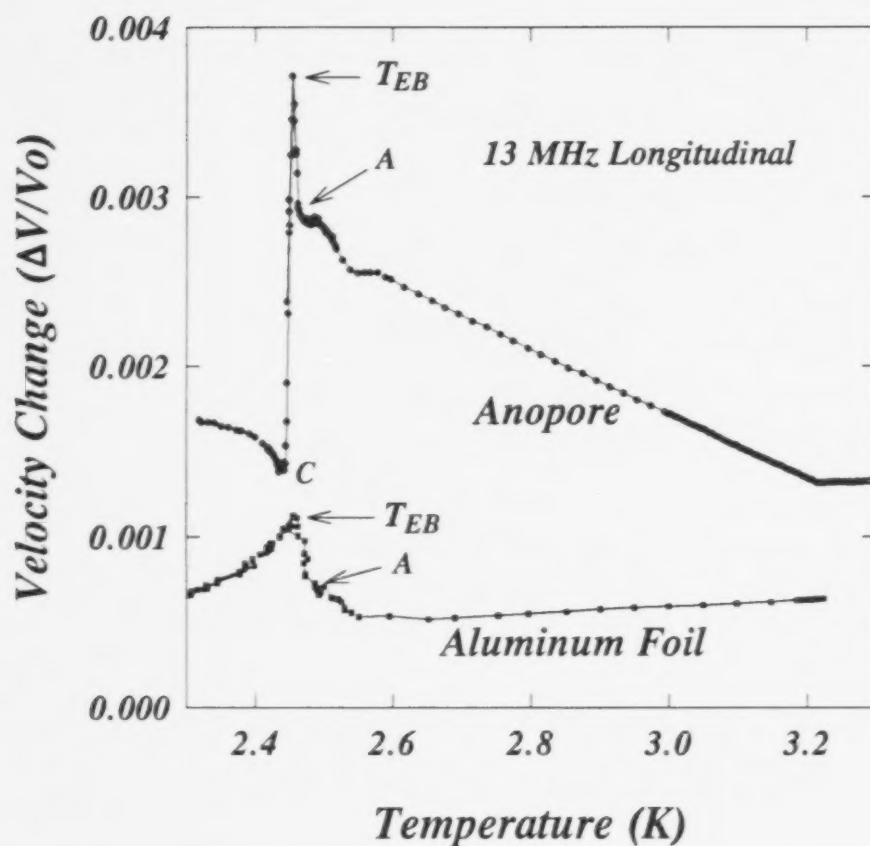


Figure 5.3.4 - Sound Velocity in Anopore and Aluminum Foil.
 The comparison between the sound velocity in Anopore and aluminum foil during bulk freezing shows that point A and the velocity peak are associated with bulk freezing while the velocity drop below T_{EB} and point C are associated with freezing the pores.

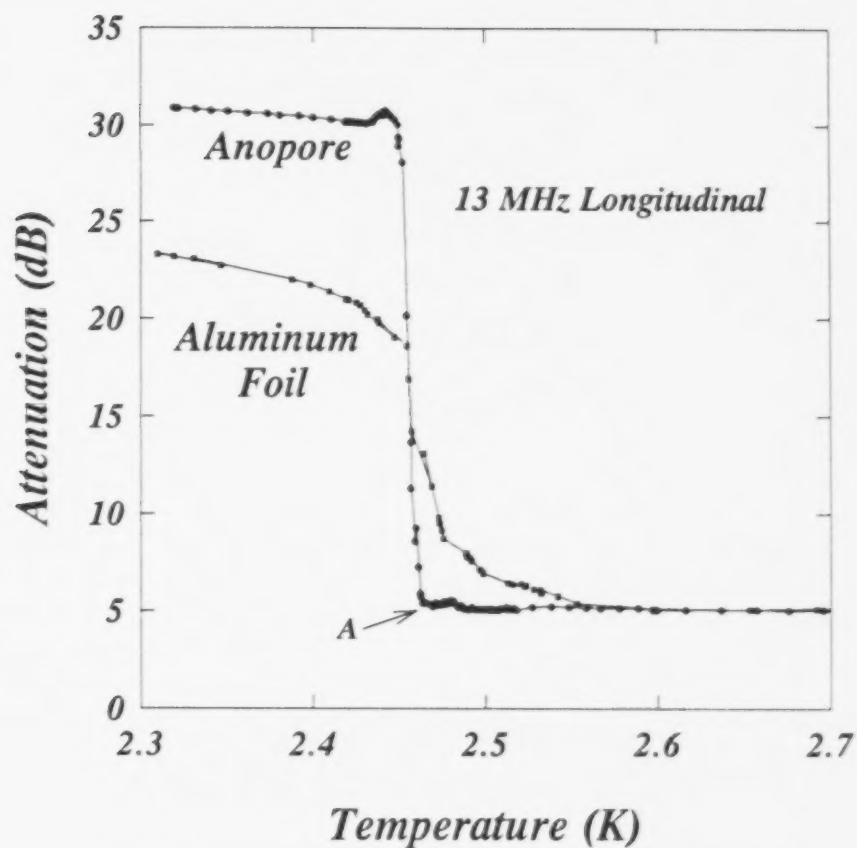


Figure 5.3.5 - Sound Attenuation in Anopore and Aluminum Foil
The comparison in the sound attenuation in Anopore and aluminum foil during bulk freezing shows that both have sharp increases near the completion of bulk freezing.

in Anopore is taking place in the aluminum foil.

The comparison between the aluminum foil and the Anopore Membrane can be summarized as follows. The increase in sound speed throughout bulk freezing is associated only with liquid leaving the pores. The features of the sound velocity in Anopore and aluminum foil are very similar above T_{EB} and so are interpreted to be bulk effects involving the replacement of surrounding liquid with solid. Freezing in the pores thus occurs below T_{EB} and is responsible for either the rapid decrease in sound speed between T_{EB} and point C or the kink at point C.

Given this information, the effect of freezing in the pores can be predicted. Once all helium in the pores has solidified, the density of the confined helium must return to its value at T_{SB} . The associated velocity decrease is the same as the previously calculated and observed increase during bulk freezing, 0.0015. The validity of this argument hinges, of course, on pressure equilibrium between bulk and confined solid helium being maintained. The characteristic time for deformation of solid helium under stress over the length of half the Anopore thickness (30 microns) is less than a second [9]. No pressure gradients between the inside and outside of Anopore can be maintained in these experiments and the original density should be recovered from the solidification process. Meanwhile, an upper bound on the velocity increase due to the modulus increase is found using the analog of equation 2.9 for the longitudinal case. As a value for the compressional modulus for a solid plate of alumina (κ_s) is not available, the κ_p/κ_s term was ignored. Using bulk values for liquid and solid helium moduli at 50 bar yields a maximum velocity increase of 0.0009. The increase taking into account the κ_p/κ_s is

probably only a small fraction of this. Therefore, unlike Vycor and silica aerogel which have much smaller elastic constants, freezing in the pores of Anopore should only be seen as a sound velocity decrease.

Taking into account the results from the comparative Vycor and aluminum foil samples, and the previous calculation, the freezing process in the pores must be occurring during the velocity decrease immediately below T_{EB} . This implies two effects not seen in Vycor or silica aerogel. First, solid helium wets the surface of the Anopore Membrane much better than the previous glasses (Vycor and silica aerogel). This is demonstrated by freezing in the pores starting indistinguishably close to T_{EB} . In other words, minimal undercooling is observed. Second, the point of the completion of freezing can be identified as point C, where the sharp drop in sound velocity ends. The complete solidification process then takes place in a 10 mK range, not surprising given the narrow band of pore sizes centered around 2000 Å.

The frequency-dependence of the longitudinal sound velocity during the transition is displayed in Figure 5.3.6. The three frequencies, 5.5 MHz (triangles), 9 MHz (squares), and 13 MHz (circles), are superimposed at point A. The height of the velocity peak is about the same for each. However, the drop in sound speed between T_F and T_{Fc} systematically decreases as the frequency is increased. This may involve coupling between the Anopore surface and the bulk solid helium. If bulk solid helium a half wavelength thick on both sides of Anopore were to suddenly contribute to the sample mass, the velocity would change 0.05, much larger than any observed effect. Still, similar frequency-dependent features were observed for the sound velocity in the

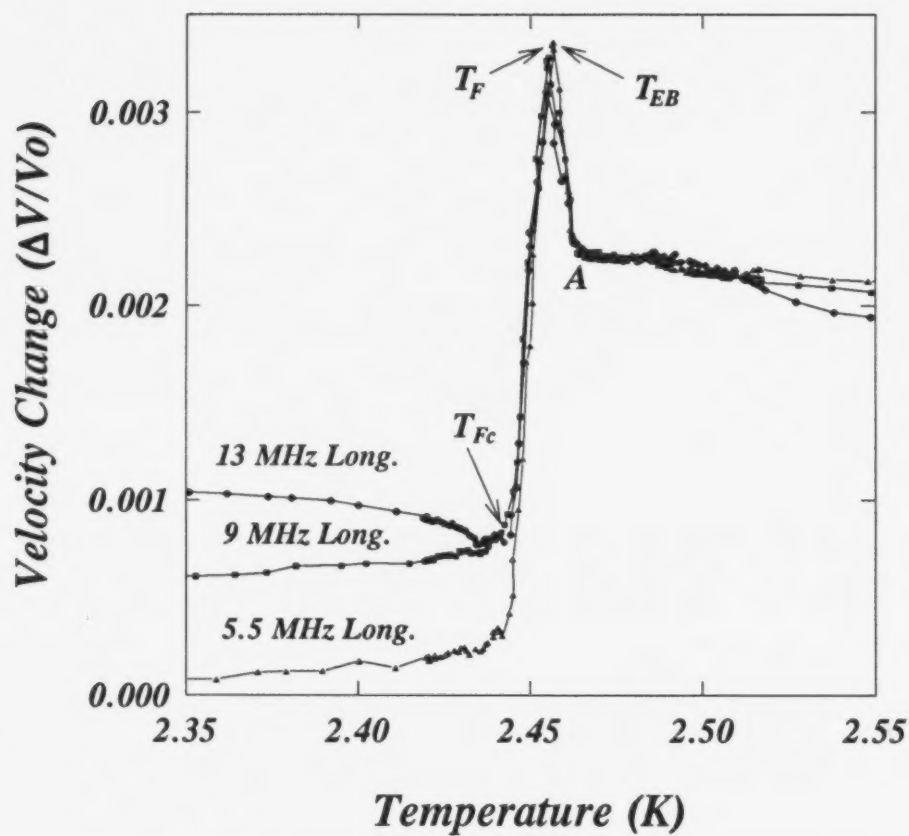


Figure 5.3.6 - Frequency-Dependence of the Freezing Transition. Sound velocity for the L(1) mode at 5.5, 9, and 13 MHz shows that the velocity change between T_F and T_{Fc} systematically increases with frequency.

aluminum foil at the completion of bulk freezing. The behavior of the sound below T_{Fc} is also markedly different. After freezing has completed, the 5.5 MHz sound velocity monotonically decreases. Conversely, the 13 MHz sound speed increases noticeably just below T_{Fc} before flattening as the temperature is reduced.

The sound velocity through the transition for 13 MHz longitudinal mode and 15 MHz shear mode are compared in Figure 5.3.7. The obvious difference between the two is that the shear wave lacks the velocity peak at T_{EB} . Instead, the sound velocity drops at point A. In the S(0) mode, the surface of the Anopore moves in the plane of the membrane with no local changes in the thickness. The bulk solid helium must couple differently than to the L(1) mode and effectively reduce the sound speed. At T_{EB} , the sound velocity decreases more rapidly. As for the longitudinal mode, the completion of freezing in the pores is very sharp (T_{Fc}). Also like the longitudinal mode, the slight velocity increase below T_{Fc} is present in the shear mode at 15 MHz.

The freezing transitions of helium in Anopore at three different pressures are displayed in Figure 5.3.8. Curves A through C are all 13 MHz longitudinal sound velocity cooling curves. The general shape of all curves is the same as previously displayed. Even for the lowest temperature transition, Curve A, there is a clear signature of the completion of freezing in the pores (T_{Fc}). Clearly, the velocity decrease between T_p and T_{Fc} gets systematically smaller for higher transitions. This reflects the dramatic increase in the sound velocity in solid helium with pressure. That is, the compressional modulus of the helium in the pores increases with pressure more rapidly than the density. At high enough pressure, the sound velocity should actually increase

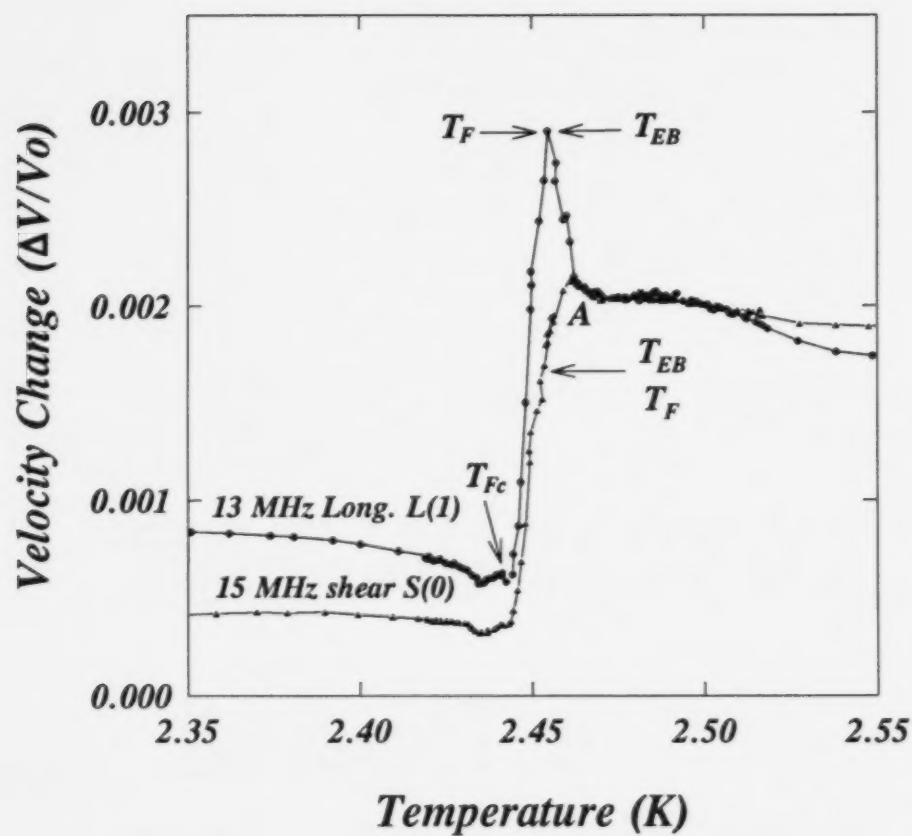


Figure 5.3.7 - Shear and Longitudinal Modes During Freezing Transition in Anopore. The sound velocities for S(0) and L(1) modes are compared. Unlike the L(1) mode, the velocity of the S(0) mode decreases between point A and T_{EB} . The fractional velocity decrease between T_F and T_{Fc} is within a about a factor of two for these two modes.

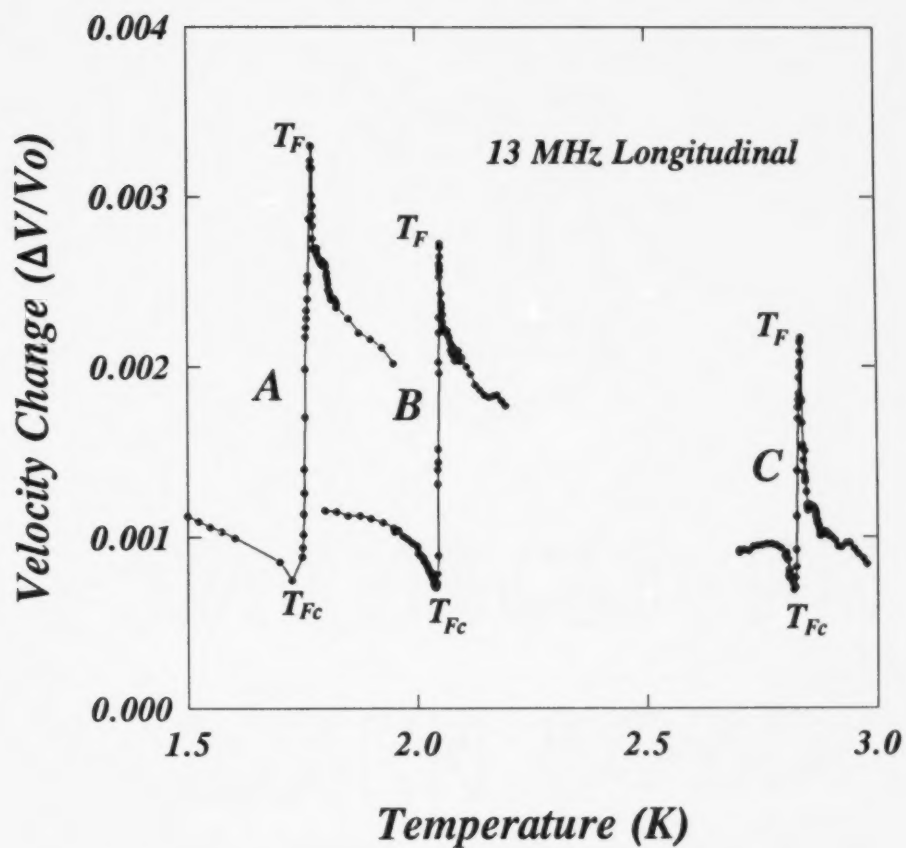


Figure 5.3.8 - Pressure-Dependence of Freezing Transition in Anopore. Sound velocity for the 13 MHz longitudinal mode shows that the velocity change between T_F and T_{Fc} decreases with increased pressure.

between T_F and T_{Fc} .

The last aspect of freezing helium in Anopore was to test for hysteresis between freezing and melting. Since there is minimal undercooling and freezing occurs over only a 10 mK range, little hysteresis is expected. Early results at high pressure indicated this to be the case. However, when scans were done closer to the melting curve minimum an interesting effect is seen. Figure 5.3.9 includes melting data for Curves A and B in Figure 5.3.8 and freezing and melting data for a still lower pressure curve, labeled A*. Curve A*, where bulk freezing is complete at about 1.62 K, shows clear hysteresis with melting temperatures higher than freezing, as in Vycor and aerogel. The range of freezing for Curve A* is larger than those at higher pressures, slightly more than 25 mK. On warming, melting begins about 13 mK higher than the end of freezing. This 13 mK hysteresis remains through most of melting. Finally, when about two thirds of the velocity increase associated with melting has occurred, the melting and freezing curves begin to converge and eventually reattach at the velocity peak. Discrepancies above the peak are due to bulk effects. Curve A, with T_{EB} at 1.77 K, has smaller but still noticeable hysteresis. Although the freezing process occurs over about 10 mK in Curve B, no hysteresis on melting is observed to within temperature control. The lack of hysteresis in high pressure curves cannot be explained entirely by a narrower freezing process. If in Curve B like Curve A*, the hysteresis were half of the range of freezing, there would be 5 mK separation between freezing and melting. Five mK should be very visible. Instead, at high pressure at least, hysteresis between freezing and melting is suppressed in Anopore Membranes. To further illustrate, Figure 5.3.10 is the sound

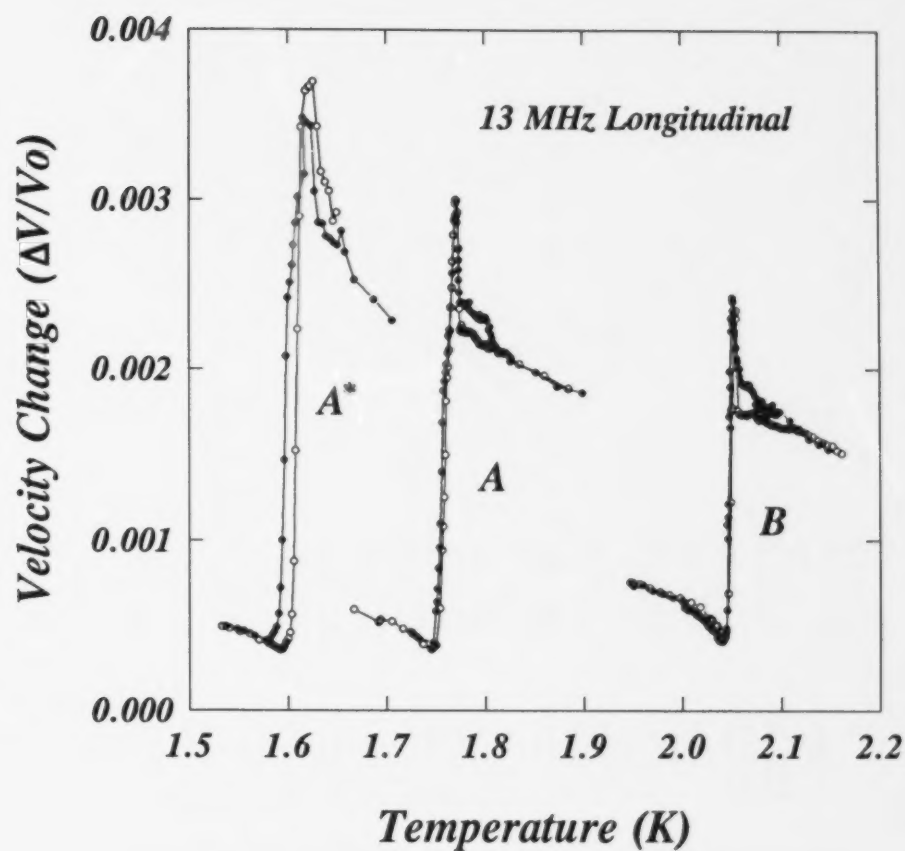


Figure 5.3.9 - Freezing and Melting in Anopore at Various Pressures. The sound velocity shows clear hysteresis between freezing and melting at low pressure (Curve A*) and minimal hysteresis between freezing and melting at higher pressure (Curve B).

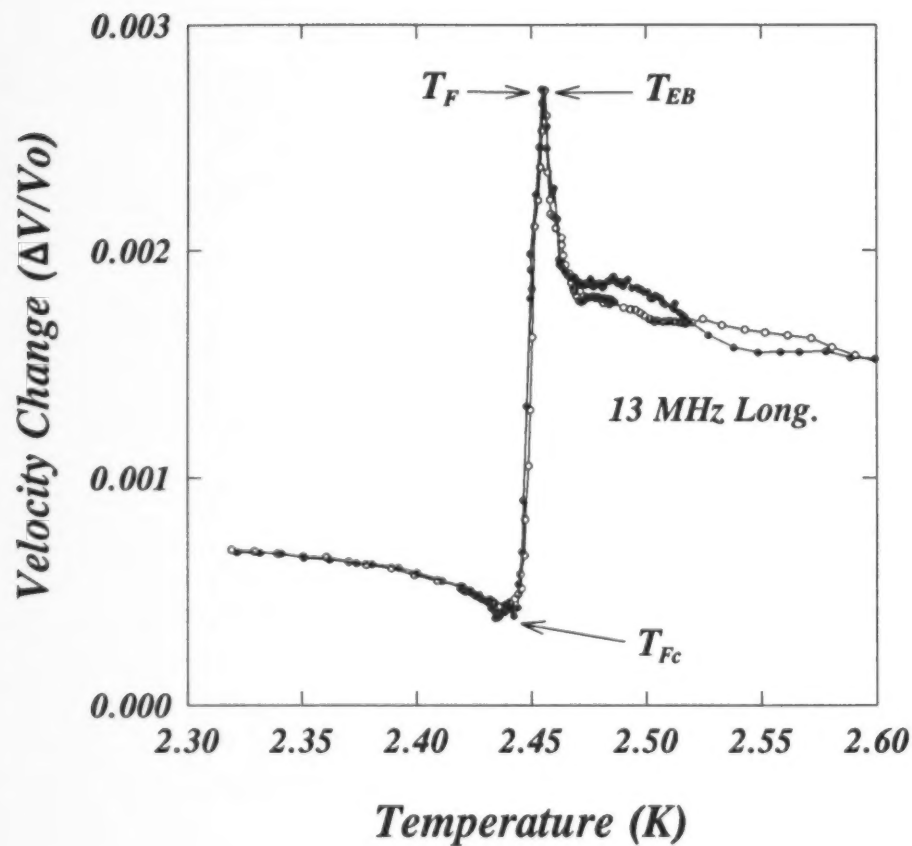


Figure 5.3.10 - Freezing and Melting in Anopore at Elevated Pressure. The sound velocity during freezing and melting in Anopore at higher pressure than Figure 5.3.8 show minimal hysteresis below T_F .

velocity for Figure 5.3.1 including melting data. Melting traces freezing to within the experimental resolution. At still lower pressure, the freezing process in Anopore Membranes should broaden even further and perhaps, at low enough pressure, remain incomplete even at the lowest temperatures. Several attempts were made to examine this behavior. Unfortunately, huge loading effects were observed when bulk freezing completed below about 1.5 K. Attenuation levels drifted as much as 5 dB and the noise levels in the sound velocity increased by orders of magnitude even after stabilizing at the desired temperatures. This made scans of freezing and melting worthless. Eventually, experimentation near the freezing curve minimum was abandoned and one scan at saturated vapor pressure was performed to observe superfluidity in Anopore and compare the decoupling for the shear and longitudinal modes.

Before exploring superfluidity in Anopore, some of the main features of freezing should be reviewed. Unlike Vycor and aerogel, there is essentially no undercooling although it is expected in 2000 Å pores, suggesting that solid helium wets the surface of the Anopore at least somewhat. The freezing in the pores occurs over a finite temperature range and is seen as a sound velocity decrease. However, unlike Vycor and silica aerogel, there is a clear point that is identified as the completion of freezing (T_{Fc}). No hysteresis between freezing and melting is observed in high pressure although some hysteresis clearly occurs when freezing in the pores begins below 2 K.

The lambda transition in Anopore may be difficult to observe in these measurements since the orientation of the pores should result in a high tortuosity, particularly for the S(0) mode. However, for the L(1) mode, the displacement of the

Anopore normal to the surface should allow some superfluid to decouple.

Figure 5.3.11 shows the sound velocity in helium-filled Anopore at saturated vapor pressure with the cell completely filled. The top curve is a scan over the entire temperature range for the 13 MHz longitudinal mode (hollow circles) and the two lower curves are enlargements of the superfluid transition region for the 13 MHz longitudinal mode and the 15 MHz shear mode (solid circles). Consider the 13 MHz entire scan first. There is a sharp velocity increase at 2.17 K clearly associated with superfluidity. The total velocity change by 1.0 K is only about 0.0005, considerably less than that of the total density effect if all liquid helium decoupled. In fact, ignoring modulus contributions, such a velocity change corresponds to a decoupling of only about 3% of the helium. The high tortuosity prevents complete decoupling of superfluid. The lambda temperature in Anopore is obviously very near that of bulk (2.176 K). Given that superfluidity in aerogel, with largest voids sizes probably 5 to 10 times smaller than those of Anopore, is suppressed 30 mK, superfluidity in Anopore should be suppressed only 5 mK or less below bulk. Distinguishing between superfluidity in the pores and in bulk is difficult for a few reasons. Even using the enlargements, picking the precise lambda temperature is difficult. Velocity changes are on the order of one part in 10^5 within a few hundredths of a degree of the transition. Noise levels are comparable to these velocity changes. Also, the calibration of the thermometer is only accurate to within 5 mK at this temperature. Still, superfluidity in the pores rather than a bulk effect appears to be responsible for the sound velocity behavior. If this were a bulk effect involving decoupling external liquid helium, only liquid within a viscous penetration

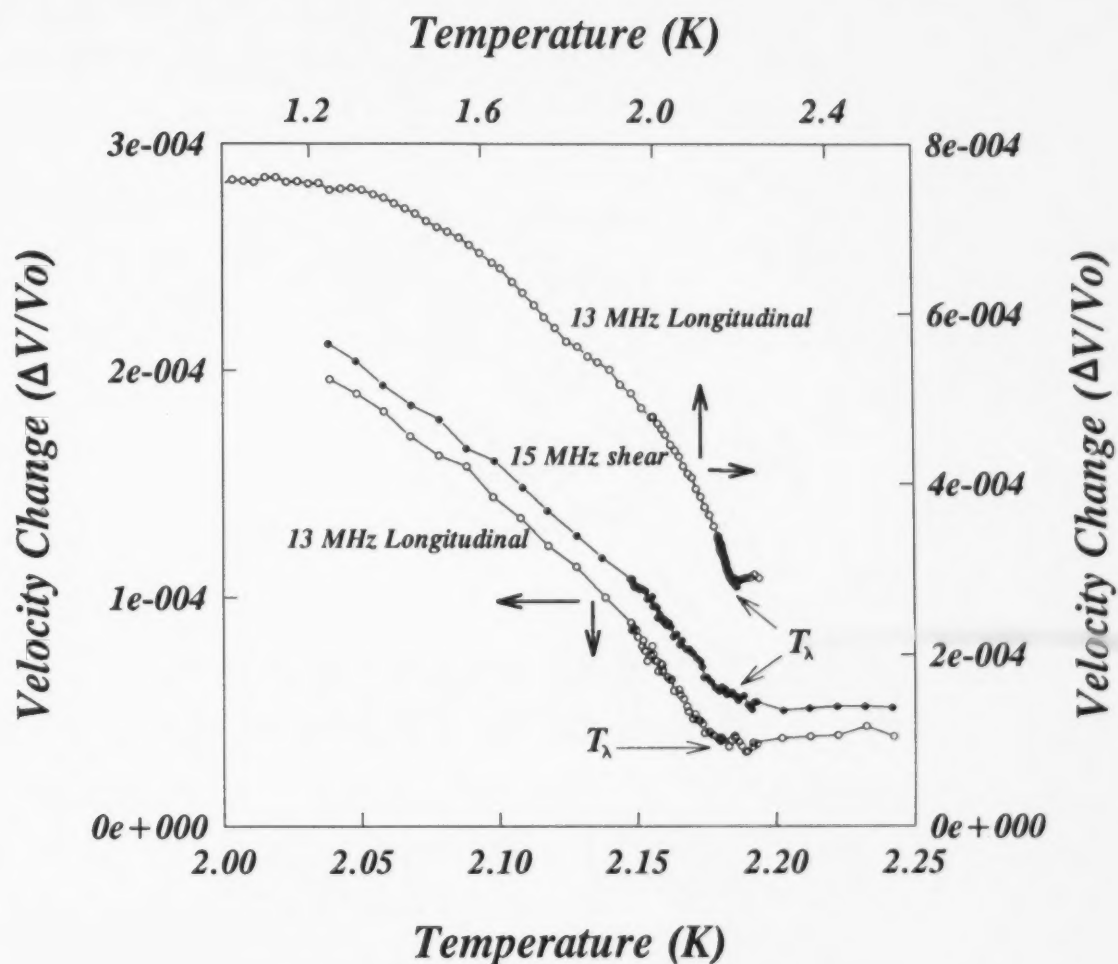


Figure 5.3.10 - Superfluidity in Anopore at Saturated Vapor Pressure. Sound velocity for the 13 MHz longitudinal mode during superfluidity in Anopore has a 0.0005 velocity change. The transition temperature is indistinguishable from that of bulk to within experimental resolution. The amount of superfluid decoupling is comparable for the shear mode.

depth ($400 \text{ \AA}$ at 10 MHz) of the surface of the sample should contribute to the shear mode. The total velocity change is much greater than would be expected for decoupling of a viscous penetration depth. Surprisingly, the sound velocity change for the shear and longitudinal modes appears to be nearly the same size for these frequencies even though the mechanism for the decoupling of superfluid for the shear mode is not clear.

CHAPTER 6 - CONCLUSIONS

The goal of this research was to study how the freezing and melting of helium in porous media depend on the pore microstructure. Porous Vycor, silica aerogel, and Anopore Membranes have widely varying pore geometries and thus make good materials for a comparative study. To see this, consider how the following well known features of solidification in pores relate to the pore microstructure. The liquid phase in small pores is metastable below bulk melting temperatures and thus undercools. From the Gibbs-Thomson model for homogeneous nucleation, the amount of undercooling, or elevated pressure in the case of helium, before solidification starts depends on the inverse pore size. Nominal pore sizes in Vycor, aerogel, and Anopore Membranes are orders of magnitude apart.

Freezing in pores occurs gradually, over a broad temperature range, even for

fluids with a triple point. This effect may be related to the undercooling. No matter how precisely prepared, these porous materials must have some distribution of pore sizes. In the Gibbs-Thomson model, solidification should start in the largest pores and continue into progressively smaller pores and corners of pores as the temperature is reduced. Aerogel has a wide range of pore sizes from 40 Å to perhaps 400 Å. In contrast, Anopore is produced with almost cylindrical pores with nearly all pore diameters within 10% of the 2000 Å mean.

There is hysteresis between freezing and melting in porous materials. The temperature of the completion of melting is higher than the onset of freezing but still less than bulk, indicating that the liquid phase is not simply being supercooled. The irreversibility may involve the interconnected nature of the pores that allows solid regions in neighboring pores to unite during growth. Anopore differs from Vycor and aerogel in that most of its pores are noninterconnected, independent from all others.

Other specific questions involving helium in pores remain from previous experiments and were explored in this research. Heat capacity experiments measured latent heats of helium in Vycor to be less than those for helium in bulk [12-13]. This was interpreted as meaning that a fraction of the confined helium remained liquid to lowest temperatures, even when freezing starts well above the Vycor freezing curve minimum. Also, the onset of freezing is very sharp in pores. This is surprising considering the often complicated microstructure of these materials and probably indicates an abrupt upper bound in the distribution of pore sizes. Finally, torsional oscillator experiments on superfluidity in Vycor under pressure produced a puzzling

result [14]. At about 25 bar the total period change associated with the decoupling of superfluid began to decrease. By about 47 bar, no decoupling was observed. This was interpreted as indicating that the superfluid density in Vycor decreases above 25 bar and eventually disappears. Thus, during the course of this research, the amount of liquid helium remaining at the lowest temperatures and where, if ever, complete freezing occurs, the sharpness of the freezing transitions, and the amount of superfluid decoupling were of interest.

Consider the pore sizes of the examined porous media as compared to the amount of undercooling. Although larger pores probably exist, Vycor necks have been measured to be 40 Å. Meanwhile, pores in aerogel and Anopore Membranes are, respectively, about one and two orders of magnitude larger than those of Vycor. The results in Chapter 5 are in reasonable qualitative agreement with equation 4.5 which predicts the amount of undercooling is proportional to the inverse pore size. After leaving the bulk melting curve at 50 bar, there is about 0.7 K of undercooling in Vycor. Under the same conditions, helium in aerogel undercools about 0.2 K. Meanwhile, helium in Anopore Membranes hardly undercools at all although a finite amount is expected in 2000 Å diameter pores. This suggests that solid helium nucleates in better contact with the surface of Anopore than with the surface of glass. Using equation 4.8, a value for the expected excess pressure for Vycor can be calculated. At 0 K, the freezing curve of helium in Vycor is about 11.0 bar higher than the bulk melting curve. The largest pores in Vycor are estimated at 60 Å and v_s is assumed to be like that of bulk, about 21 cm³/mole. A calculation of the molar volume change between the solid and liquid helium

in pores ($v_i - v_l$) should account for the volume of the inert monolayer or two against the pore wall since it is presumably already solid. Assuming 28 micromoles of helium per square meter of Vycor make up this inert layer [37], then 32% of the Vycor pore volume does not contribute to the molar volume change during freezing. The molar volume change is then calculated to be 0.83 cc/mole [11]. The interfacial energy for bulk hcp solid helium was measured to be 0.16 erg/cm². Using these values yields an excess pressure of 20 bar, almost twice that of measured value. This calculation can easily have a factor of two error given the large uncertainty of the interfacial energy, pore size, and change in molar volume. In addition, no radius of curvature effects or any solid wetting the pore wall have been considered in this simple calculation.

As an overview of the hysteresis, typical sound velocity and attenuation curves during freezing and melting in each porous medium are compared in Figures 6.1 and 6.2. The graphs on both pages are ordered from bottom to top: Vycor, aerogel, and Anopore. As before, T_F and T_M are the start of freezing and completion of melting in the pores while T_B is the completion of bulk freezing. The hysteresis in Vycor and aerogel is very similar. In Vycor at this particular filling, T_F , T_M , and T_B occur at 1.82 K, 2.18 K, and 2.47 K, respectively. In silica aerogel (at a slightly lower pressure), T_F , T_M , and T_B occur at 2.11 K, 2.19 K, and 2.27 K, respectively. Thus, T_M is about halfway between T_F and T_B for both Vycor and silica aerogel.

Anopore is markedly different. At the lowest pressure (Curve A) in Figure 5.3.8, the hysteresis occurs over a 25 mK range and during most of melting there is 13 mK of hysteresis between freezing and melting. However, this behavior ceases at higher

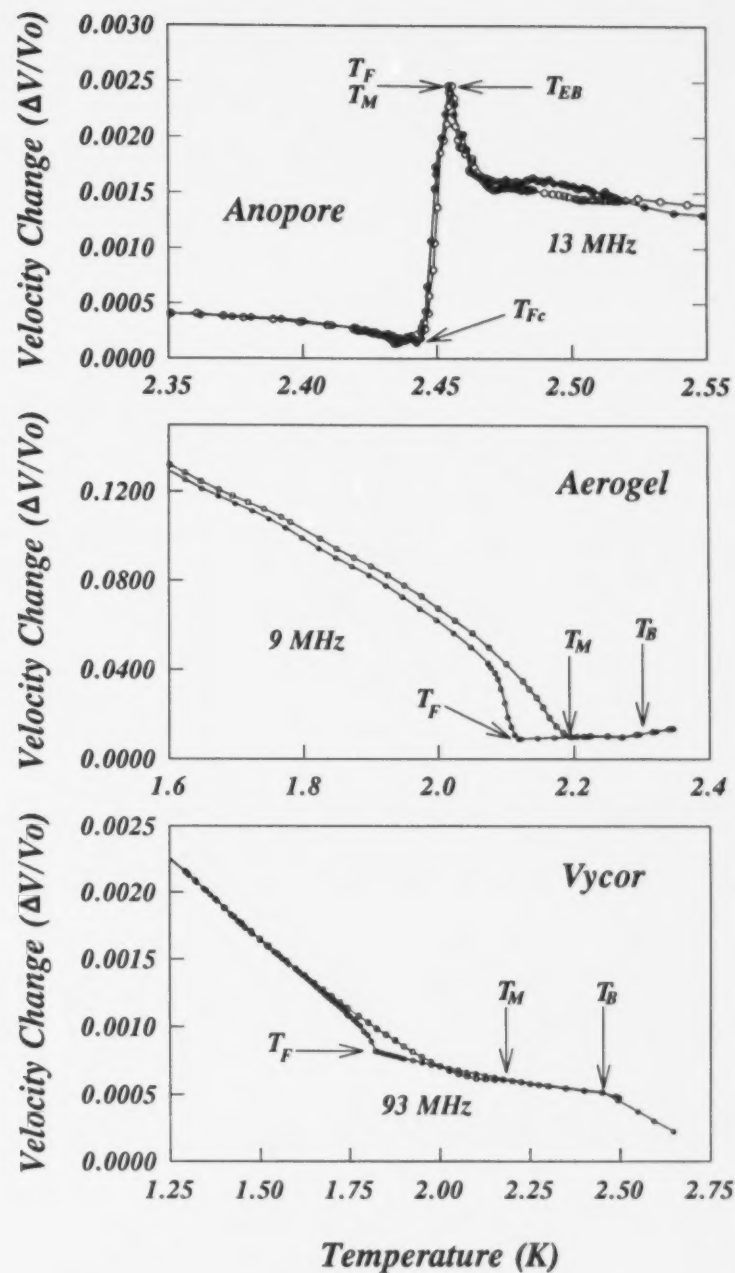


Figure 6.1 - Hysteresis Region in Porous Media

The sound velocity compares the hysteresis between freezing and melting in Vycor, silica aerogel, and Anopore Membranes.

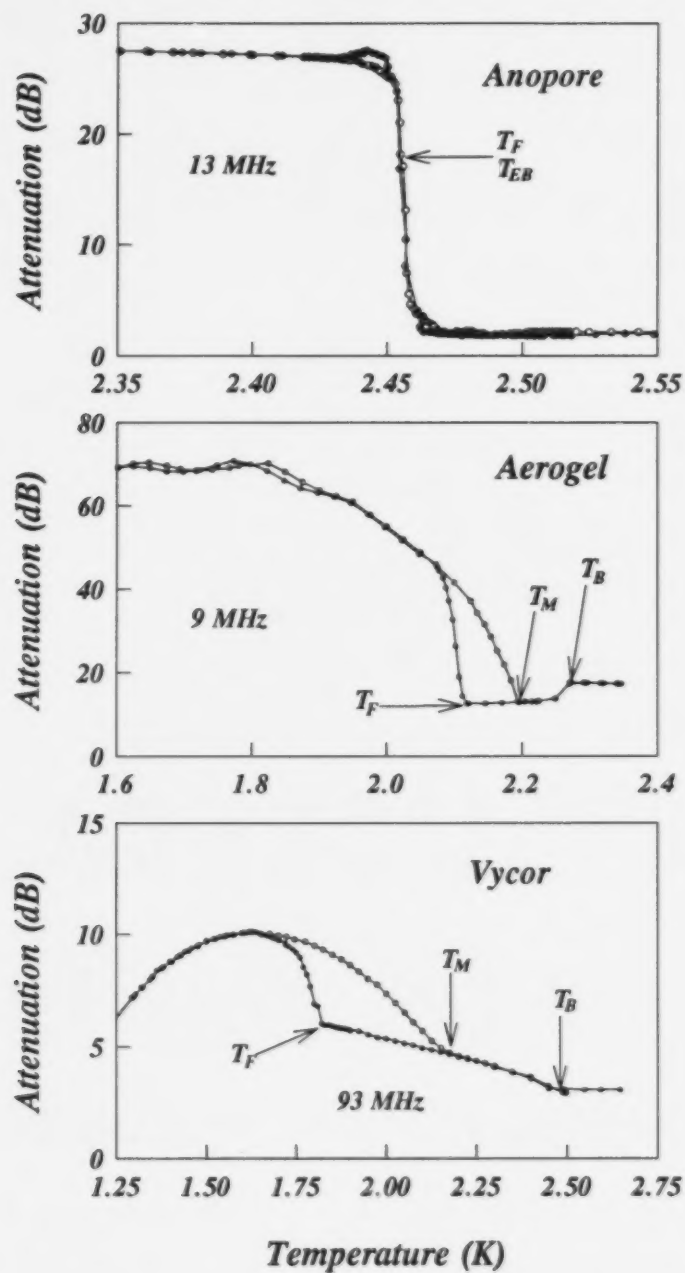


Figure 6.2 - Hysteresis Region in Porous Media

The sound attenuation compares hysteresis between freezing and melting of helium in Vycor, silica aerogel, and Anopore Membranes.

pressure. In Figure 6.1, freezing begins at 2.455 K immediately below the completion of bulk freezing, and is complete at 2.444 K so solidification process occurs over 11 mK. Thus, about 5 mK of hysteresis is expected during melting. Instead, minimal hysteresis is observed. At pressure well above the melting curve minimum, hysteresis in Anopore Membranes is suppressed.

The noninterconnected nature of the pores in Anopore may be responsible for the near reversibility of freezing and melting. To review this mechanism, picture solid droplets forming in the largest pores minimize free surface energy. As the temperature is reduced, solid grows into the corners of these largest pores and also forms in separate, smaller pores. Freezing and melting at this point should be reversible. Eventually, solid from neighboring voids unites, reducing the liquid-solid surface area but possibly forming a grain boundary. Such an event would create a more energetically stable solid and melting temperatures would be higher. A typical pore in Anopore, unlike those in Vycor and aerogel, is not connected to the others. Thus, uniting of solid regions to reduce the surface free energy, is only possible within an isolated pore. At a given temperature, the solid phase is then not significantly more stable on warming than on cooling and hysteresis between freezing and melting would be much smaller.

The sharpness of the freezing onset in Figures 6.1 and 6.2 and the range over which freezing then continues are both related to the pore size distribution. For Vycor and silica aerogel, the onset of freezing (T_F) and completion of melting (T_M) are very sharp, suggesting that there is an abrupt upper bound of pore sizes. This is surprising for silica aerogel. For a particular silica aerogel, nitrogen adsorption experiments were

done [57]. The fraction of the total pore volume made up by given sized pores decreased above 200 Å and slowly approached zero around 500 Å. (The pore size distribution for a given silica aerogel is highly dependent on its preparation. The silica aerogel used in these experiments may differ to some degree.) Only in Anopore is the completion of freezing or the onset of melting discernable, where the flat portion meets the steep changes in sound velocity about 10 to 30 mK below T_F depending on where T_F occurs. This suggests that Anopore Membranes also have a sharp lower bound of pore sizes while Vycor and aerogel have a more gradual distribution of smaller pores.

Given that melting temperatures are higher than freezing temperatures, the completion of freezing of helium in Vycor and aerogel is probably near the onset of hysteresis on warming. In Vycor, this occurs about 0.15 K below T_F . In aerogel, hysteresis in sound velocity begins as low as 0.7 K below T_F although the hysteresis region in attenuation is much smaller. Clearly, this demonstrates that Anopore has the narrowest pore size distribution while aerogel has the broadest.

Comments on the fraction of liquid remaining in the pores after freezing has started can be made based on these results. Displayed in Figure 5.1.10 are sound velocity curves of helium at low pressure in Vycor. Curve A has only the superfluid transition at 1.45 K and no solidification in pores. The total velocity change between T_λ and 0 K is 0.0020. Curves B-G, which left the bulk melting curve at increasing pressures, have freezing transitions in the pores at increasing temperatures. For curves B through F, the total sound velocity change of any curve between T_λ and 0 K is smaller than the preceding curve. This must be a recoupling effect of solid helium replacing

superfluid helium in Vycor. In the pressure range of curves B-F, 35.9 to 36.7 bar, confined helium at 0 K has both solid and liquid components and the frozen fraction systematically increases. However, for curve G, done at 37.4 bar, the total velocity change between T_λ and 0 K is larger than that of curve F. This probably represents nearly the pressure where all helium in the Vycor pores freezes.

Figure 5.2.9, freezing in aerogel at a variety of pressures, must be interpreted differently than Figure 5.1.10 but yields similar results. Curve F has only the superfluid transition in aerogel at 1.74 K. Here, unlike Vycor, although recoupling of solid helium occurs, solidification in aerogel increases the total sound velocity change between T_λ and 0 K. In fact, increasing the solidification pressure and thus T_F monotonically increases this velocity change. In curves E to D, the velocity change increases rapidly for small pressure increases. Eventually, around curve B, done at 29.95 bar, the relative velocity changes between T_λ and 0 K become consistent with the pressure dependence of the modulus of solid helium. Thus by 30.7 bar, only about 0.70 bar over the minimum required to initiate freezing, most or all of the confined helium in aerogel has solidified.

Thus, the interpretations are consistent with those of pressure measurements of helium in Vycor [11]. Except in a small pressure range above the minimum for solidification, all the confined helium does freeze. Latent heat and molar volume changes less than in bulk cannot be explained by a liquid helium component in the pores at lowest temperatures.

Figures 5.1.10 and 5.2.9 also indicate that the superfluid density in the pores does not decrease as the pressure is increased above the bulk melting minimum in contrast to

the interpretations of previous torsional oscillator experiments. In the pressure range, the amount of decoupling appears to be about the same for each scan. Further, the amount of helium that decouples in these figures is greater than at SVP in both Vycor and aerogel. This is expected since the density of the liquid helium in the pores is considerably larger at these pressures than at SVP.

Some final comments should be made on the phase-diagrams for helium in Vycor and aerogel. In each case two curves were constructed: freezing and melting of helium in the pores. However, only the freezing curve may be a true coexistence curve where equilibrium thermodynamics apply. What is meant by this is that no matter how the freezing curve is approached from the liquid state (cooling, in this case, or pressurizing), solidification should only start on this curve. The melting curve, particularly near the flat portion, may be highly path dependent. Consider that the melting curve flattens at the same pressure as the freezing curve. Clearly, to melt any solid in the pores requires raising the temperature by a finite amount. However, the constructed melting curve implies that lowering the pressure at constant temperature must immediately melt all solid. Clearly, this is not expected. Rather a finite pressure decrease should be needed to melt all solid. Thus, the melting curve flattening at the same pressure may be an artifact of the way the experiment is performed.

The point where the lambda line meets the freezing curve in pores should affect the slope of the freezing curve. First consider bulk helium, whose heat capacity diverges at the superfluid transition. The rate of change of the liquid's entropy is therefore maximum at superfluid transition temperature. Recall that the slope of the helium

melting curve (dP/dT) is described by the Clausius-Clapeyron equation which includes the liquid entropy:

$$\frac{dP}{dT} = \frac{s_l - s_s}{v_l - v_s} \quad 6.1$$

Here s_l and s_s are the liquid and solid molar entropies and v_l and v_s are the liquid and solid molar volumes. Assuming the entropy of the solid phase of helium has negligible temperature dependence compared to the liquid phase, the point on the melting curve with the maximum curvature is the tricritical point. That is, where the lambda line reaches the bulk melting curve.

Similarly, heat capacity measurements of helium in aerogel and Vycor at SVP have been made. The heat capacity of helium in aerogel [20] resembles bulk in that there is a sharp cusp-like singularity at the superfluid transition. Therefore, assuming the Clausius-Clapeyron equation can be used, the temperature of maximum curvature in the helium freezing curve in aerogel should occur at the tricritical point. On the other hand, the heat capacity of helium in Vycor has a rounded peak that occurs about 0.15 K above the superfluid transition. The point of maximum curvature in the helium freezing curve in Vycor should be about 0.15 K above the tricritical point.

Data from helium freezing curves in Vycor (Figure 5.1.11) and aerogel (Figure 5.2.11) were fit to fourth order polynomials so that the temperatures of maximum

curvature (3rd derivative equals zero) can be compared to the tricritical points. For helium in Vycor, the calculated point of maximum curvature (1.48 K) is indeed above the tricritical point (1.41 K), in qualitative agreement with heat capacity results. For helium in aerogel, where the two points should coincide, the point of maximum curvature (1.73 K) is only slightly above the tricritical point (1.71 K). These calculations have considerable uncertainty but show the tendencies expected from the heat capacity results.

In summary, the amount of undercooling, the behavior of the hysteresis, the sharpness of freezing transitions, and the broadness of the freezing process are related to the characteristics of these porous media. There appear to be particular pressures above which all helium in these porous media solidifies. Finally, superfluid density in Vycor and aerogel above the bulk melting curve is higher than at SVP and remains nearly constant until the helium freezes.

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